MECHANISMS OF THE DESTABILIZATION OF KAOLINITE CLAY SUSPENSIONS WITH ALUMINUM SULFATE

By

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Abstract of Dissertation Presented to the Graduate Council in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

MECHANISMS OF THE DESTABILIZATION OF KAOLINITE CLAY SUSPENSIONS WITH ALUMINUM SULFATE

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Three major experimental approaches were used in this study to elucidate the mechanisms involved in the specific aluminum-clay interactions and subsequent destabilization of dilute kaolinite clay suspensions: (1) In one series the dosage of aluminum sulfate was maintained at some selected constant value while the final pH of the suspension was varied from 3 to 10. (2) In another series the final pH of the suspension was maintained at a constant value of 3, 5 or 8 with the aluminum sulfate dosage varying from 1 mg/l to 50 mg/l. (3) In a series of kinetic experiments both the time of mixing and the intensity of agitation were varied.

Neither aluminum adsorption nor charge reversal of clay particles was demonstrated at pH 3 within the limits of the aluminum sulfate dosage used. However, the electrophoretic mobility of the clay particles was found to be reduced to a constant minimum value as the dosage of aluminum sulfate increased. Consequently, the mechanism involved in the destabilization of kaolinite clay suspensions at this pH value is believed to be due to a reduction of the repulsive potential between the

negatively charged clay particles through compression of the electrical double-layer, which in turn is due to the incorporation of hydrogen and hydrated metallic aluminum ions into the Gouy diffuse layer.

At pH 5, a very narrow zone of coagulation was found at the isoelectric pH point which marked the beginning of a charge reversal zone with the subsequent restabilization of the suspension as the dosage of aluminum sulfate increased. The Freundlich adsorption isotherm model was found best to describe the adsorption of the hydrolyzed aluminum polynuclear complex ions by the kaolinite clay particles. Therefore, it is postulated that the mechanism of the destabilization at this pH value is a reduction of the zeta potential of the clay particles through the specific adsorption of the hydrolyzed aluminum polynuclear complex ions onto the clay surface, with the subsequent reduction of the surface potential of the clay particles.

It is shown from the experimental results that at pH 8 physical enmeshment might account for the mechanism of the destabilization of the kaolinite clay suspensions when rapid and abundant precipitation of aluminum hydroxides occurs, i.e., when the dosage of aluminum sulfate exceeds 40 mg/l. However, when the dosage of aluminum sulfate is less than 40 mg/l at this pH, a mechanism of mutual coagulation between colloidal aluminum hydroxides and clay particles better describes the phenomena of the destabilization.

In all cases investigated, the residual turbidity curve as a function of the time of mixing shows that the turbidity could be reduced to a constant minimum value by stirring the suspension system with a

total of 2,000 paddle revolutions. The constant minimum value of the residual turbidity appears to be dependent on such factors as the final pH of the suspension, the aluminum sulfate dosage, the intensity of agitation and the clay concentration.

The effect of the initial clay concentration on the destabilization process was found to follow Smoluchowski's theory at pH 3 and pH 5, whereas it had little effect at pH 8 when the aluminum sulfate dosage was higher than 50 mg/l.

I. INTRODUCTION

The need of scientific control for the removal of natural clay turbidity from the raw water of public water supply systems has for many years been a challenging problem in the field of water chemistry. In order to provide a sound solution to this problem, the mechanisms involved in the destabilization of clay suspensions must be clearly demonstrated. Therefore, the present research has been initiated in an attempt to elucidate the mechanisms by which an inorganic coagulant effects the destabilization of dilute clay suspensions under controlled conditions.

Aluminum sulfate has been widely and effectively used as a coagulant to remove clay turbidity from water for many years. The mechanisms involved have been investigated and several theories have been proposed. However, due to the lack of specific controls in the investigations and a good understanding of the chemistry of aluminum, the proposed mechanisms have had to be revised through the years, and as yet are not well established.

Electrophoretic techniques have been used throughout this study in an attempt to reveal any significant relationships between the electrophoretic mobility measurements and the residual turbidity data, and also to elucidate the charge reversal phenomena due to the adsorption of the aluminum hydrolysis products.

II. HISTORICAL REVIEW

Before the turn of the century, water treatment employing coagulation was an art and not a science. The early patents of that period contain no definitive data or present even the simplest of the reactions involved. As the water works industry began to grow to meet the needs of a rapidly expanding population, increased emphasis was placed upon both bacteriological and chemical quality. In 1914, the first quality standards to apply to water used on interstate carriers were developed, and in 1923-25 the U.S. Public Health Service initiated what were really the first definitive studies of water coagulation. They were done by **Theriault**, Clark and Miller, and published in Public Health Reports.[1-6] They concluded that:

1. there must be present a certain minimum quantity of aluminum or ferric cation in the water being coagulated;

2. they called attention to the applicability of the Schulze-Hardy rule and pointed out that an anion of strong coagulating power, such as sulfate ion, should be present;

3. they found that the hydrolysis products of both aluminum and ferric sulfate were not pure hydrates but contained combined sulfate and that in consequence the pH must be properly adjusted.

In 1928, Bartow and Peterson[7] published their studies on the effect of some selected salts on the rate of coagulation and the optimum precipitation of alum floc. Some of the salts studied were found to

broaden the pH range of rapid coagulation toward the low pH side.

In 1928, in a very important paper which remained unnoticed for many years, Mattson[8] was able to demonstrate the relationship between the microelectrophoretic mobility of colloidal particles and the aluminum salt dosage. Mattson found that the positively charged sol, formed by the hydrolysis of the aluminum salt, exhibits its greatest effect on the zeta potential of the clay particle at a pH of about 5.2. He further showed that the hydrolysis products of aluminum and ferric salts are more effective than the trivalent metallic ions, Al^{+++} and Fe^{+++}, in reducing or neutralizing the zeta potential of the colloidal particles.

Black and his associates (1933-34) initiated the use of a pilot plant and refined jar test techniques to demonstrate the effect of some selected ions on the pH zone of rapid coagulation.[9-11] They found that the zone of rapid floc formation was considerably broadened on the acid side by the sulfate ion and to a much lesser degree by the chloride ion. Further, using both ferric sulfate and ferric chloride, they showed that in the pH zone from 6.5 to 8.5, floc formation was markedly retarded or even inhibited. They ascribed the existence of this zone to the reversal of the charge on the floc, and emphasized that adsorption is an important mechanism of turbidity removal.

In 1949, Langelier and Ludwig[12] made some basic studies on the mechanisms of flocculation, using synthetic clay suspensions, and came to the conclusion that the base exchange capacity and the size of clay particles were important factors in the flocculation process. They were perhaps the first workers to distinguish between the terms coagulation,

which they characterized as "perikinetic" and flocculation, which they called "orthokinetic" coagulation. For the first time, they used the term "binder alum" to characterize its bridging functions in floc formation.

In 1959, Pilipovich et al.[13] reintroduced the long neglected microelectrophoretic technique to the study of water coagulation. They investigated the effects of pH, alum dosage, zeta potential, and base exchange capacity of clay particles on the coagulation of clay suspensions with alum, and concluded that the optimum coagulation dosage for clays with low base exchange capacity is lower than that for clays with high base exchange capacity. They further confirmed Mattson's[8] view that the hydrolysis products of aluminum salts are more effective than the trivalent metallic aluminum ion, Al^{+++}, in producing good coagulation.

Black and Hannah[14] summarized the results of their electrophoretic studies on the coagulation of three synthetic clay suspensions with aluminum sulfate as follows:

> The zeta potential of clay particles was found to be dependent on the pH and on the alum dosage. An amount of alum equivalent to several times the base exchange capacity of the clay suspension was required to neutralize the particle charge. Clarification was best in the range pH 7.5 - 8.5 where the particles were negative, rather than at pH values where the particle charge had been neutralized. Fair coagulation was often obtained below pH 4.5 where the particles were nearly neutral. In many instances, residual turbidities changed sharply without any accompanying change in mobility values.

In a series of five papers, Packham presented his extensive studies on the coagulation of dispersed clays with aluminum salts.[15-19] He concluded that anions have a great effect on the pH range of optimum coagulation, while cations have very little influence except under

conditions wherein they can produce insoluble hydroxides. Packham also concluded that the mechanism of the coagulation of dilute clay suspensions with aluminum salts is simply a physical enmeshment of the clay particles by the precipitation of the insoluble aluminum hydroxide. Thus, he came to another conclusion, namely that those factors which bring about the maximum precipitation of aluminum hydroxide will also bring about the optimum coagulation of clay suspension.

Matijevic et al.[20-23] employed microelectrophoretic mobility measurements in their studies of coagulation and for the characterization of the hydrolysis products of Al^{+++}. They applied the well-known Schulze-Hardy rule in demonstrating that the predominant species of the product of aluminum hydrolysis in the acid range is a tetravalent octanuclear complex, $Al_8(OH)_{20}^{++++}$. They further showed, by using both coagulation techniques and microelectrophoretic techniques, that the hydrolyzed aluminum species can reverse the charge of the negatively charged silver halide sols, AgI and AgBr, while the hydrated trivalent metallic aluminum ion cannot. This charge reversal was found to coincide with the optimum coagulation of silver halide sols. Matijevic et al. have asserted that the hydrolyzed aluminum species are more strongly adsorbed than the trivalent aluminum ion.

In 1962, Mackrle[24] confirmed his hypothesis that the initial phase of coagulation is accomplished by the following successive steps:

1. the hydrolysis of coagulant added;
2. the crystallization of the aluminum or ferric hydrous oxides;
3. the compensation of the negative charges on the colloidal

particles;

4. the mutual coagulation of the hydrous oxides and the colloidal impurities in the water; and

5. the formation of "microflocs."

These microflocs are then removed from the water by the agglomeration or mutual collision of the particles. He further showed that the zeta potential is pH-dependent, and that the low zeta potential zone of the hydrous oxides identified the pH range of the optimum coagulation.

Stumm and Morgan (1962) reemphasized the importance of chemical theory in their explanation of the basic mechanisms of colloid stability and coagulation.[25] From their studies of the alkalimetric titrations of aluminum in the presence of various ion groups, such as phosphate, pyrophosphate, oxalate and salicylate, they concluded that for certain anions specific chemical equilibria, such as complex formation, may be more important than double-layer compaction through counter ion adsorption. However, if the anions are weak coordinators with the coagulating metal ions, the compacting of the diffuse part of the double layer generally will be more important than chemical interaction for the destabilization of colloids. In addition to alkalimetric titration studies, they also suggested a laboratory technique for coagulation study which allows constant pH and alkalinity to be maintained throughout each experiment, thus facilitating the interpretation of specific chemical effects in a coagulation process.

In the studies of turbidity removal with ferric sulfate, Black and Walters[26] again demonstrated the significant effect of the base exchange

capacity of the clay on the coagulant dosage for producing charge reversal at low pH range, although the base exchange capacities of the clay suspensions were not found to be directly or proportionally related to the coagulant dosage which is required to accomplish satisfactory coagulation. Further, they gave strong support to the view that the "overdosed isoelectric point" marks the beginning of the zone of efficient orthokinetic coagulation, or flocculation.

Kim et al.[27] investigated the effects of cation exchange capacity, pH and alkalinity on the coagulation process and concluded that:

1. The optimum final pH of coagulation depends upon the initial alkalinity present in the suspension. As the alkalinity of the suspension is increased, the optimum final pH decreases.

2. The optimum final pH of coagulation is independent of alum dosage, but the pH range for good coagulation broadens with increasing alum dosage.

3. When the cation exchange capacity of the suspension is greater than about 10 μe/l, a pH value near the isoelectric point favors coagulation.

4. Low concentration (less than 100 ppm) kaolinite suspensions can best be treated by maintaining pH at an isoelectric point that is a function of suspension alkalinity.

Based on recent studies of the coagulation and flocculation of several river sediment suspensions with aluminum sulfate, Black and Chen[28] postulated that both coagulation and flocculation are strongly controlled by the properties of the coagulant. The characteristics of clay particles,

such as base exchange capacity, particle size, total surface area and particle charge density, may influence the coagulant dosage required to achieve a good coagulation, but not the basic mechanisms of coagulation and flocculation for a particular coagulant. They further suggested that different mechanisms of destabilization are involved in various pH zones which are controlled by the hydrolytic reactions of aluminum ion.

Tambo[29] fully discussed the validity of double-layer theory for understanding and controlling the stability and the instability of colloidal suspensions. He further emphasized that the critical zeta potential is without doubt not only a definite value but is dependent on the conditions of the suspension. There exist two factors to control the critical zeta potential; (1) the kinetic energy of a suspended particle, and (2) the maximum interaction energy. Based on the assumption of the existence of a critical zeta potential in the coagulation of natural water, Tambo showed that the measurement of the zeta potential, i.e., electrophoretic studies of coagulation, is one of the most important tools for investigating and controlling coagulation.

The effect of particle size on the destabilization of colloidal suspensions in water has been extensively studied by Vilaret.[30] As a result of his investigation he demonstrated the following several phenomena:

1. The optimum coagulating and flocculating dosage of a cationic polymer increases directly with an increase in the total surface area of the system, which in turn is inversely proportional to the size of the suspended particles.

2. No optimum dosage was observed during coagulation with non-hydrolyzing metal ions, and thus particle size has no marked effect on the required coagulant dosage.

3. When a hydrolyzing coagulant, such as aluminum sulfate, is used, the particle size has an effect on the required dosage, although the relationship has not been so well defined as with high polymers.

4. Particle size has a definite effect on the kinetics of the destabilization process with the time required for optimum destabilization decreasing with decreasing size of suspended particles.

III. THEORETICAL CONSIDERATIONS

Chemistry of Aqueous Aluminum

Since any explanation of the basic mechanisms of colloid stability and coagulation, either by chemical theory or physical theory, should concern itself with the chemical composition of the coagulant being used, a comprehensive exploration and understanding of the chemistry of aluminum is very essential for the present investigation. It is believed that the chemistry of aluminum in very dilute aqueous solutions (less than 10^{-4} mole/liter) is very different from that of high concentrations. Therefore, the present discussion will be limited to solutions having a concentration range of 10^{-6} mole/liter to 10^{-4} mole/liter, which is in the practical range encountered in water coagulation.

Hydrolytic Reactions of Aluminum Ion

When aluminum ion is present in dilute aqueous solution, it is very easily hydrolyzed, and the hydrolytic reactions are very complicated. Brosset et al.[31,32] investigated the hydrolysis of aluminum ion, Al^{+++}, by potentiometric titration techniques and concluded that in the acid range the main product of Al^{+++} hydrolysis is a polynuclear complex with a stoichiometric ratio of OH^- to Al(III) of 2.5:1. With reference to the behavior of aged solutions and crystallographic evidence, they suggested that the trivalent polynuclear complex $\left(Al_6(OH)_{15}\right)^{+++}$ is the most likely main product. On the other hand, in the alkaline range the assumption of

the existence of a single complex $[Al(OH)_4]^-$ and solid $Al(OH)_3$ explains the Brosset data[31] very well.

Based on the ionic strength effect of the Schulze-Hardy rule, Matijevic and his coworkers[21] initiated the use of the critical coagulation concentration of aluminum salt solutions for silver iodide sols (both aged and in statu nascendi) and silver bromide sols (in statu nascendi) for determining the actual charge of ionic species in solution. By using the new electrolytic coagulation techniques they were able to identify the main hydrolysis products between the possible complexes, such as $[Al_6(OH)_{15}]^{+++}$ and $[Al_8(OH)_{20}]^{++++}$, all of which have a stoichiometric ratio of OH^- to Al(III) of 2.5 to 1. They postulate the polynuclear tetravalent species $[Al_8(OH)_{20}]^{++++}$ as the most likely formula of the complex in the pH range 4 to 7. However, at pH values below 4, the critical coagulation concentration corresponds to that of trivalent counterions indicating the presence of the simple hydrated aluminum ion.

In addition to the complexes $[Al_6(OH)_{15}]^{+++}$ and $[Al_8(OH)_{20}]^{++++}$, more highly polymerized and hydrolyzed aluminum ions containing 6, 7, 10 or even 13 aluminum atoms in the complex, such as $[Al_7(OH)_{17}]^{++++}$ and $[Al_{13}(OH)_{34}]^{+++++}$, have been postulated by several other investigators.[33,34,35]

Frink and Peech[36] propose a completely different picture, in postulating that the hydrolysis of the aluminum ion in dilute aqueous solutions proceeds according to the simple monomeric hydrolysis mechanism, $Al^{+++} + H_2O \rightleftarrows Al(OH)^{++} + H^+$. They further attempt to show that, without controlling pH, aluminum hydroxide $Al(OH)_3$ begins to

precipitate upon diluting the solution to a concentration of aluminum salt lower than 10^{-5} mole/liter, which is considered to be the critical value of the supersaturation of $Al(OH)_3$.

Packham suggested two functional types of reactions which are thought to be involved in aluminum hydroxide precipitation as follows:[18]

1. Ligand exchange reactions.

$$[Al(H_2O)_6]^{+++} + H_2O \rightleftarrows [Al(H_2O)_5(OH)]^{++} + H_3O^+ \quad (1a)$$

$$[Al(H_2O)_5(OH)]^{++} + H_2O \rightleftarrows [Al(H_2O)_4(OH)_2]^{+} + H_3O^+ \quad (1b)$$

$$[Al(H_2O)_4(OH)_2]^{+} + H_2O \rightleftarrows [Al(H_2O)_3(OH)_3] + H_3O^+ \quad (1c)$$

$$[Al(H_2O)_3(OH)_3] + H_2O \rightleftarrows [Al(H_2O)_2(OH)_4]^{-} + H_3O^+ \quad (1d)$$

$$[Al(H_2O)_6]^{+++} + X^{--} \rightleftarrows [Al(H_2O)_4 X]^{+} + 2H_2O \quad (2)$$

$$[Al(H_2O)_4(OH)_2]^{+} + X^{--} \rightleftarrows [Al(H_2O)_4 X]^{+} + 2OH^- \quad (3)$$

2. Olation reactions.

$$2\,[Al(H_2O)_5(OH)]^{++} \rightleftarrows \left[(H_2O)_4\,Al\begin{matrix}OH\\OH\end{matrix}Al(H_2O)_4\right]^{++++} + 2H_2O \quad (4a)$$

$$[(H_2O)_4Al(OH)_2Al(H_2O)_4]^{++++} + H_2O \rightleftarrows [(H_2O)_4Al(OH)_2Al(H_2O)_3(OH)]^{+++} + H_3O^+ \quad (4b)$$

$$\left[(H_2O)_4Al(OH)_2Al(H_2O)_3(OH)\right]^{+++} + \left[Al(H_2O)_5(OH)\right]^{++}$$

$$\rightleftarrows \left\{(H_2O)_4Al\begin{matrix}OH\\OH\end{matrix}\begin{matrix}H_2O\\Al\\H_2O\end{matrix}\begin{matrix}OH\\OH\end{matrix}Al(H_2O)_4\right\}^{+++++} + 2H_2O \qquad (4c)$$

Table 1 shows the composition of several of the ionic and molecular species which have been suggested for aluminum and equilibrium constants for the reactions by which they may be formed.

Table 1

Hydrolysis Equilibria of Aluminum

No.	Equilibria	Log of Equilibrium Constant* (25°C)	References
1	$\left[Al(H_2O)_6\right]^{+++} + H_2O \rightleftarrows \left[AlOH\right]^{++} + H_3O^{+}$ **	-5.03	37
2	$2Al^{+++} + 2H_2O \rightleftarrows \left[Al_2(OH)_2\right]^{+++} + 2H^{+}$	-6.27	37
3	$Al^{+++} + 3H_2O \rightleftarrows Al(OH)_3(S) + 3H^{+}$	-9.10	38
4	$Al(OH)_3(S) + H_2O \rightleftarrows \left[Al(OH)_4\right]^{-} + H^{+}$	-12.74	38
5	$8Al^{+++} + 20H_2O \rightleftarrows \left[Al_8(OH)_{20}\right]^{++++} + 20H^{+}$	--	21
6	$6Al^{+++} + 15H_2O \rightleftarrows \left[Al_6(OH)_{15}\right]^{+++} + 15H^{+}$	-47.00	32
7	$Al(OH)_3(S) \rightleftarrows Al^{+++} + 3OH^{-}$	-32.96	39

*Additional constants can be found in the works by Bjerrum, Schwarzenbach and Sillen,[40] and Latimer.[41]

**Ligand - H_2O molecules are ommitted from subsequent reactions for brevity.

Figure 1 is a general plot of the concentrations of the various aluminum species at different pH values. The solubility of aluminum hydroxide $Al(OH)_3$ is defined by the boundary of the shaded area on the figure.

Table 2 presents calculated data for equilibrium pH values for which the molar ratio of $[Al^{+++}]$ or $[Al_6(OH)_{15}^{+++}]$ to $[Al_T]$ has been predetermined. The reaction formula and equilibrium constant used for this calculation are listed in line No. 6 of Table 1.

Table 2

Calculated Equilibrium pH Values for Successive States in One Reaction for the Hydrolysis of Al^{+++} at Al_T.*

$\frac{[Al^{+++}]}{[Al_T]}$	$\frac{6[Al_6(OH)_{15}^{+++}]}{[Al_T]}$	pH
0.99	0.01	4.23
0.90	0.10	4.31
0.80	0.20	4.35
0.70	0.30	4.38
0.60	0.40	4.42
0.50	0.50	4.46
0.40	0.60	4.50
0.30	0.70	4.56
0.20	0.80	4.63
0.10	0.90	4.75
0.01	0.99	5.16

*A concentration of 1.5×10^{-4} mole/liter, which is equivalent to 50 mg/l of $Al_2(SO_4)_3 \cdot 18H_2O$, is assumed for $[Al_T]$ in the calculation. $[Al_T]$ is the total aluminum concentration.

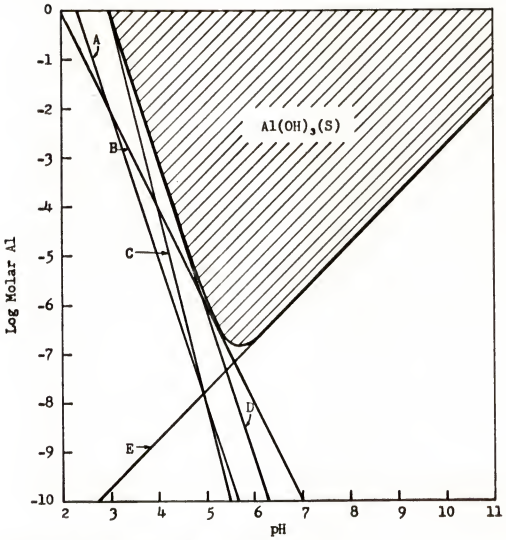


Fig. 1 - Solubility Curve for Aluminum Hydroxide.

A: $Al_6(OH)_{15}^{+3}$ D: Al^{+3}

B: $Al(OH)^{+2}$ E: $Al(OH)_4^-$

C: $Al_2(OH)_2^{+4}$

Alkalimetric Titration Curves

The information yielded from the results of the alkalimetric titrations of aluminum in aqueous solutions is very valuable for understanding aluminum hydrolysis phenomena and the composition of the various hydrolysis product species as functions of pH value. Figure 2 shows typical alkalimetric titration curves for aluminum sulfate solutions with different total concentrations of aluminum. The titration curves for aluminum sulfate solution and aluminum in the presence of sodium bicarbonate $NaHCO_3$ or sodium sulfate Na_2SO_4 solution are shown in Figure 3.

The average number of bound hydroxide ions per aluminum ion applied, the formation function $\bar{n}$, can be calculated from the data of alkalimetric titrations. The computation of the function for aluminum sulfate solution may be illustrated in the following way.

Assume that the series of aluminum hydrolysis product species can be represented by the general formula

$$\left\{Al_m(OH)_n(SO_4)_p\right\}^{3m-n-2p}$$

where m and n may equal to any small positive integral number excluding zero.

p may equal to any small positive integral number including zero.

The total aluminum concentration at any pH is given by

$$\left[Al_T\right] = \left[Al^{+++}\right] + \Sigma m\left\{Al_m(OH)_n(SO_4)_p^{3m-n-2p}\right\} \qquad (5)$$

The electroneutrality at any pH is given by

$$\left[H^+\right] + \left[Na^+\right] + 3\left[Al^{+++}\right] + \Sigma(3m-n-2p)\left[Al_m(OH)_n(SO_4)_p^{3m-n-2p}\right] = 2\left[SO_4^{--}\right] + \left[OH^-\right] \quad (6)$$

The total concentration of sulfate ion at any pH is given by

$$\left[SO_4^{--}\right] = \frac{3}{2}\left[Al_T\right] - \Sigma p\left[Al_m(OH)_n(SO_4)_p^{3m-n-2p}\right] \quad (7)$$

The combination of equations (6) and (7) leads to

$$\left[H^+\right] + \left[Na^+\right] + 3\left[Al^{+++}\right] + \Sigma(3m-n-2p)\left[Al_m(OH)_n(SO_4)_p^{3m-n-2p}\right] = 3\left[Al_T\right] - 2\Sigma p\left[Al_m(OH)_n(SO_4)_p^{3m-n-2p}\right] + \left[OH^-\right] \quad (8)$$

The combinations of equations (5) and (8) leads to

$$\left[H^+\right] + \left[Na^+\right] + 3\left[Al^{+++}\right] + \Sigma(3m-n-2p)\left[Al_m(OH)_n(SO_4)_p^{3m-n-2p}\right] = 3\left[Al^{+++}\right] + 3\Sigma m\left[Al_m(OH)_n(SO_4)_p^{3m-n-2p}\right] - 2\Sigma p\left[Al_m(OH)_n(SO_4)_p^{3m-n-2p}\right] + \left[OH^-\right] \quad (9)$$

The simplification and rearrangement of equation (9) leads to

$$\left[H^+\right] + \left[Na^+\right] - \left[OH^-\right] = \Sigma n\left[Al_m(OH)_n(SO_4)_p^{3m-n-2p}\right] \quad (10)$$

Now, the formation function $\bar{n}$ at any pH can be given by

$$\bar{n} = \frac{\left[OH^-\right]_{\text{bound}}}{\left[Al_T\right]} \quad (11)$$

$$\bar{n} = \frac{\Sigma n\left[Al_m(OH)_n(SO_4)_p^{3m-n-2p}\right]}{\left[Al_T\right]} \quad (12)$$

$$\bar{n} = \frac{\left[H^+\right] + \left[Na^+\right] - \left[OH^-\right]}{\left[Al_T\right]} \quad (13)$$

Since the parameters on the right side of equation (13) are known from alkalimetric titration data, the formation function $\bar{n}$ can be easily evaluated.

Some of the computed formation function $\bar{n}$ data are plotted as functions of pH in Figure 4.

Charge of Specific Hydrolysis Products

Since there is a random behavior in the arrangement of the structure of the hydrolysis product in the hydrolytic reactions, only the statistical charge average of the hydrolysis products can be evaluated from formation function $\bar{n}$ data. However, because the best available data indicate the existence of some active predominant hydrolysis products throughout the entire series of reactions, a general discussion of the charge of some specific hydrolysis products is feasible and it provides valuable information for an understanding of the electrokinetic characteristics of the flocs formed by the interaction of the polymeric species with clay particles in the destabilization process. The charge of the various aluminum hydrolysis products which are assumed to be formed at different pH values can be summarized in a hypothetical scheme as shown in Figure 5.

Aging Effect

When solutions of aluminum salts are aged, either at ordinary room temperatures or at elevated temperatures, certain aqua-complexes may be formed by hydrolysis of the aged solutions. These aging reactions are more rapid in solutions having higher concentration of hydroxide ion,

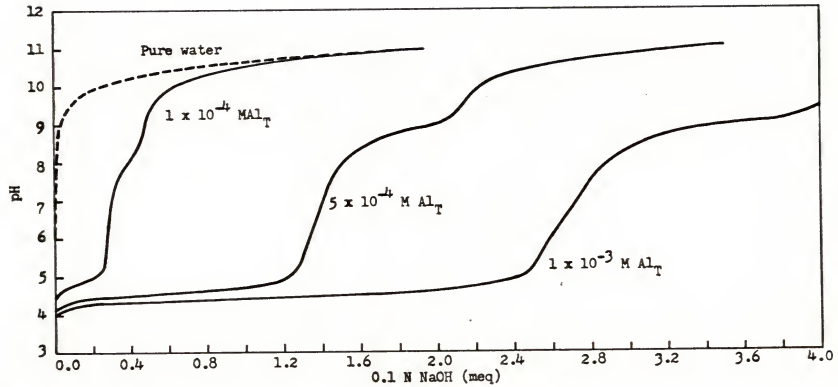


Fig. 2 - Alkalimetric Titration Curves for Aluminum Sulfate Solutions.

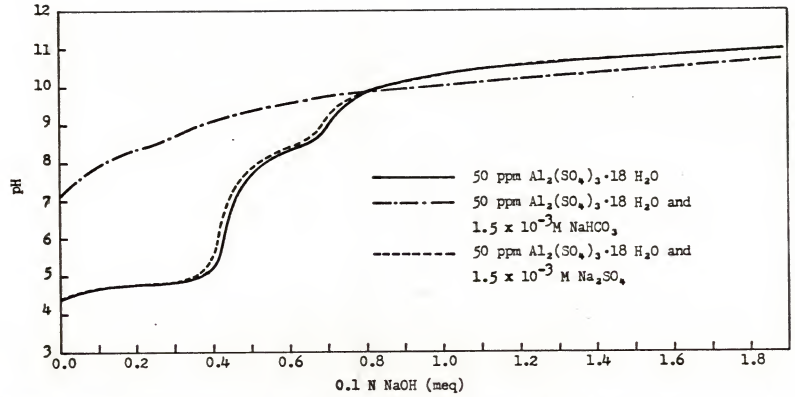


Fig. 3 - Alkalimetric Titrations of Aluminum and Aluminum in the Presence of Sodium Bicarbonate or Sodium Sulfate.

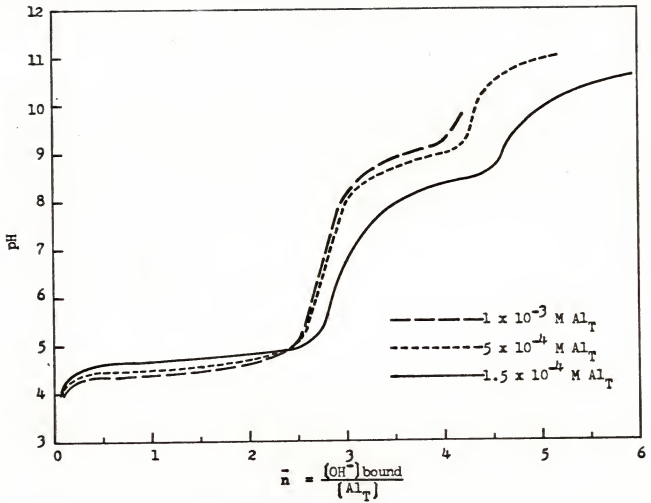


Fig. 4 - Formation Function Curves for Aluminum Sulfate Solutions.

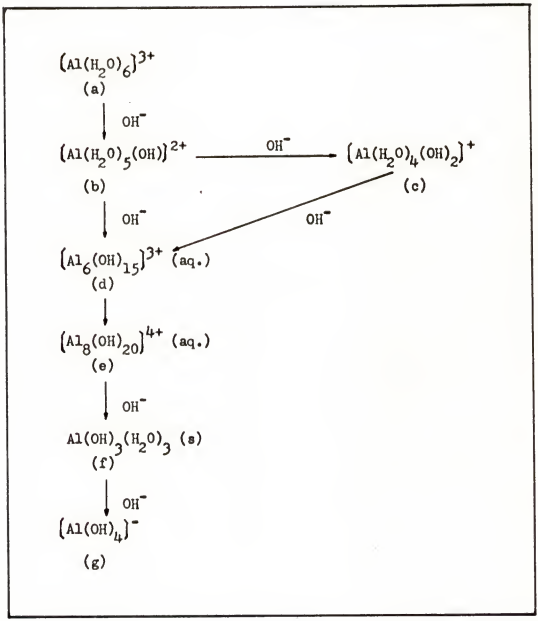


Fig. 5 - Stepwise Conversion of the Tripositive Aluminum Ion to the Negative Aluminate Ion. (From Stumm and Morgan[25])

or at elevated temperatures.[25]

It has been shown that this aging effect causes a decrease in the critical coagulating concentrations of aluminum ions and simultaneously an increase in the hydrogen ion concentration of the solutions of aluminum salts.[20] Figure 6 and Figure 7 show the effect of this aging process on the coagulating concentration and pH of aged aluminum solutions.

Complex Formation

The formation of soluble and insoluble complexes by specific chemical interactions of aluminum ions with anionic functional groups, such as sulfates and phosphates, has considerable significant effect on the flocculation process through a cross-linking or bridging mechanism.[42] It is especially important when metal ions are employed to flocculate hydrophilic colloidal suspensions.[25] Some of the complex formation reactions of aluminum ions and their equilibrium constants are listed in Table 3.

Characteristics of Kaolinite Clays

Clays comprise the major portion of the colloidal material which, suspended in natural waters, the water chemist terms natural turbidity. Langelier and Ludwig[12] were among the first to initiate the use of synthetic clay suspensions for the investigation of the water coagulation. Black and Chen have demonstrated the applicability of the results from synthetic clay suspension studies to natural river sediment suspensions.[28] Therefore, for simplicity in

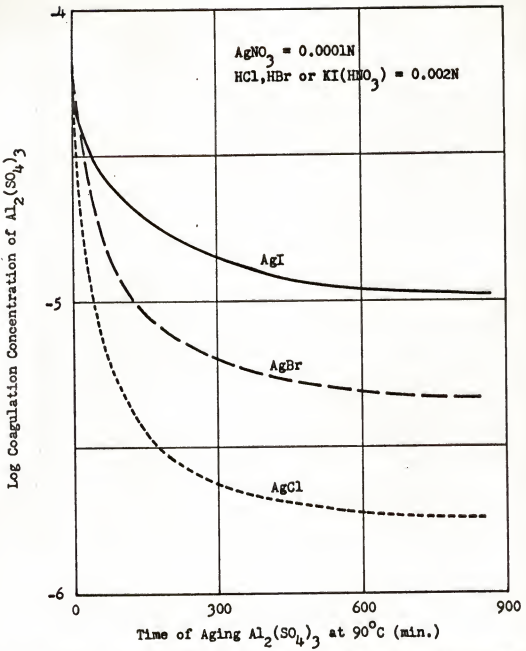


Fig. 6 - The Effect of the Time of Aging of Aluminum Sulfate Solutions at 90° on the Coagulation Values of Silver Chloride, Silver Bromide and Silver Iodide Sols in statu nascendi.(From Matijevic and Tezak.[20])

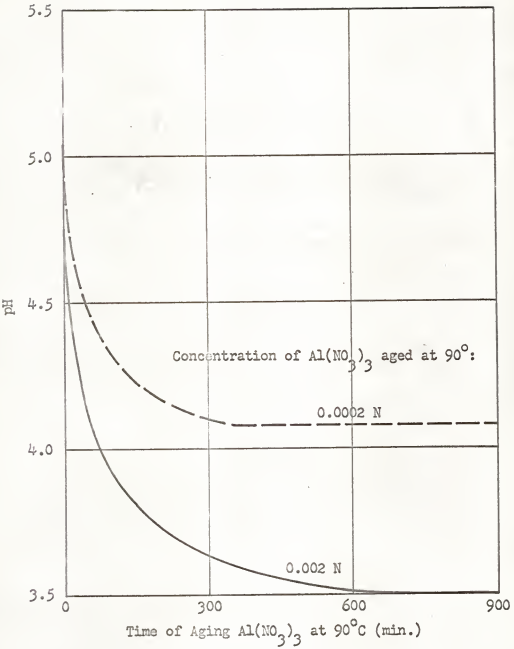


Fig. 7 - The Change of pH in Solutions of $Al(NO_3)_3$ When Aged at 90°C. (From Matijevic and Tezak.[20])

Table 3

Complex Formation Reactions of Aluminum[25]

No.	Equilibrium	Log of Equilibrium Constants (25°C)
1	$Al^{+++} + PO_4^{---} \rightleftarrows AlPO_4$ (S)	22
2	$Al^{+++} + P_2O_7^{----} \rightleftarrows [AlP_2O_7]^-$	--
3	$Al^{+++} + F^- \rightleftarrows [AlF]^{++}$	6.13
4	$Al^{+++} + 3\ Acetate^- \rightleftarrows [Al(Acetate)_3]$	--
5	$Al^{+++} + 3\ Oxalate^{--} \rightleftarrows [Al(Oxalate)]^{---}$	16.3
6	$Al^{+++} + Salicylate^{--} \rightleftarrows [Al\ Salicylate]^+$	14

designing the laboratory experiments comprising the present investigations, kaolinite clay suspensions have been used. A general description of the characteristics of kaolinite clays will therefore be useful.

Structure and Chemical Composition of Kaolinite Clays

Kaolinite may be described as a two-layer clay whose particles are made up of a single tetrahedral silicon sheet topped by a slightly distorted octahedral aluminum sheet. The two layers are joined by condensation and splitting off of water between adjoining hydroxyl groups in the vertex position. Thus a single oxygen linkage remains and is shared by the two layers, resulting in a primary valence bond between the sheets.

The atomic charges in the structural units are balanced, and the

chemical composition of a typical structural unit may be expressed as $(OH)_8Al_4Si_4O_{10}$. Kaolinite is often referred to as having a 1:1 lattice, and the extent of atom substitutions in the lattices is relatively small.[43] A schematic diagram of the crystal structure of kaolinite is shown in Figure 8.

Size and Shape of Clay Particles

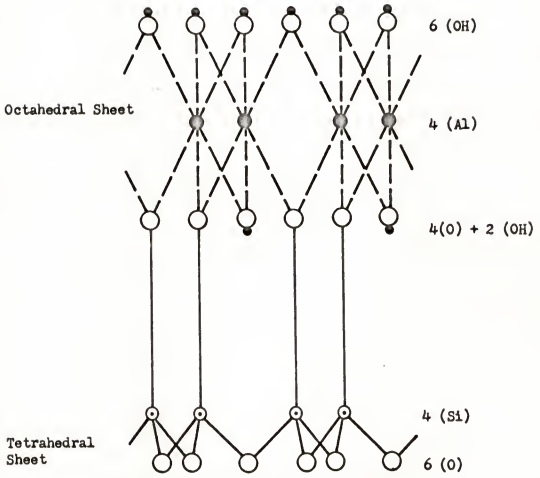
Due to the existence of the strong valence bond between the two unit layers of kaolinite clay, these clay particles commonly are quite resistant to natural mechanical cleaving forces. Consequently, natural kaolinite clays are usually composed of fairly large unit particles, larger than three microns. A kaolinite clay particle may be described as a thin, plate-like, hexagonal crystal.

Origin of Surface Charge on Clay Particles

The surface charge on clay particles, which are hydrophobic colloids, may be produced, according to van Olphen[44] in either of two ways. The first source of surface charge which he suggests is the net result of imperfections within the interior of the crystal lattice of the particle. The second source suggested is the preferential adsorption of certain specific ions on the particle surface.

Cation Exchange Capacity of Clay Particles

The cation exchange capacity of a clay is its ability to exchange cations with the solution phase. The aluminum layer in kaolinite clay seems to have amphoteric properties and will produce more hydrogen ions by dissociation as the pH of the system increases. Therefore, kaolinite



Formula of unit cell: $[Al_2(OH)_4(Si_2O_5)]_2$

Unit cell dimensions:

A = 5.15 Å

B = 8.9 Å

C = 7.2 Å

Unit cell weight: 516

Fig. 8 - Schematic Diagram of the Crystal Structure of Kaolinite Unit Cell. (From van Olphen[44]).

clays have variable cation exchange capacities depending upon the pH of the system. The cation exchange capacity of kaolinite clays may vary from 3 to 15 milliequivalents per 100 grams at pH 7.0.[45]

Adsorption Sites of Clay Particles

According to van Olphen[44] kaolinite clay has a nonexpandable lattice and thus a smaller "c-spacing." Such a structure tends to physically prevent the accommodation of cations in the interior of the clay particle. Therefore, all cations must be adsorbed on the exterior surface of the clay particle.

Mechanisms of Destabilization

In the field of colloid science at least two different theories have been historically advanced to explain the basic mechanisms involved in the stability and instability of colloidal systems. The first theory is the so-called chemical theory which assumes that colloids are aggregates of definite chemical structural units, and assumes the existence of specific chemical interactions between specific ions in both phases of colloids and solutions. According to this theory the destabilization of colloids is the result of the precipitation of insoluble complexes formed by those specific chemical interactions. The second theory, termed the physical theory or double-layer theory, emphasizes the importance of the electric double layers surrounding the colloidal particles in the solutions and the significant effects of counter-ion adsorption and zeta potential reduction in the destabilization of colloidal systems. These two theories may appear at first

sight to be different, but they are not mutually exclusive. As a matter of fact, both mechanisms must be employed in order for a comprehensive understanding and for effective control of the phenomena of colloid stability and instability. Under the present heading only a general discussion of the destabilization mechanisms of the hydrophobic colloids, to which clay colloids are classified, will be given.

Coagulation

Definition. According to La Mer[46] coagulation can be best defined as follows: "We propose that coagulation be used for the general kinetic process obeying the simple Smoluchowski equation independent of θ, whereby colloidal particles are united (L. coagulare - to be driven together) as typified by the effects of electrolytes upon gold sols. Coagulation is brought about primarily by a reduction of the repulsive potential of the electrical double layer in accordance with the ideas advanced by Derjaguin, Landau, Verwey and Overbeck."

Double-Layer Theory. The electric double-layer surrounding a colloid may be created by the preferential adsorption of counterions onto the clay surface as a result of the charge deficiency within the clay lattice, or the direct ionization of some of the molecules on the colloid surface. Among the many theories[47,48] which describe the structure of the electric double-layer, the Stern-Gouy diffuse double-layer theory has been found most acceptable in the case of clay colloid systems. In this particular model, part of the counterions remains in a compact layer, Stern layer, on the charged colloid surface in consequence of the existence of strong electrostatic forces as well as van der Waals

forces, while the other part of the counterions extends into the bulk of the solution and constitutes the so-called diffuse Gouy-Chapman layer. Figure 9 shows the structure of the Stern-Gouy double-layer and the corresponding potentials. The potential at the surface of the particle itself is generally designated as ψ_0, while the potential at the boundary between the Stern and the Gouy part of the double-layer is designated as ψ_δ. The potential at the plane of shear which essentially separates the hydration water from the bulk of solution is distinguished as the zeta, ζ, potential. It is this zeta potential which controls the stability and instability of the colloid system.

Critical Zeta Potential. According to the findings of electrophoretic studies on water coagulation,[14,28] the zeta potential of colloids need not be reduced to zero in order that coagulation may take place, and this fact has led to the concept of a critical zeta potential. The theoretical derivation of the critical zeta potential is based on the principle that the total kinetic energy, E_k, of the colloid particle should be large enough to overcome the energy barrier, which is the maximum interaction energy, E_{max}, between two approaching colloidal particles (see Figure 10). Tambo concluded from his derivation of the critical zeta potential for the coagulation of ordinary natural waters, which have inverse values of the thickness of the Debye-Hückel ionic atmosphere (κ values) in the range of $10^{5.5}$ to $10^{6.5}$ cm^{-1}, that 12 mV may be used as a threshold value for the coagulation of most waters in water supply systems.[29] Figure 11 shows his critical zeta potential as a function of κ value.

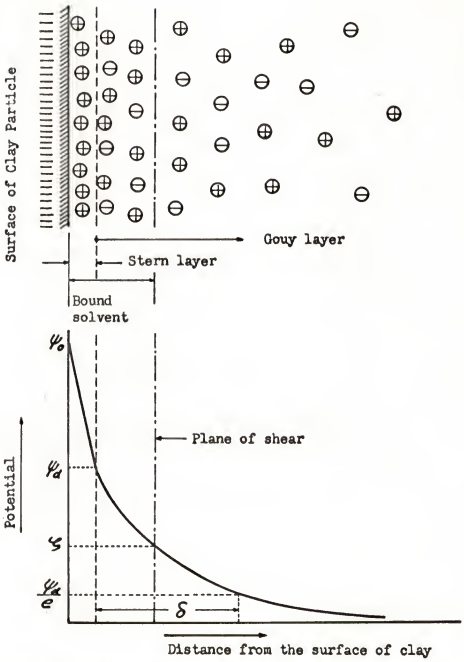


Fig. 9 - The Structure of Stern-Gouy Double Layer and the Corresponding Potentials.

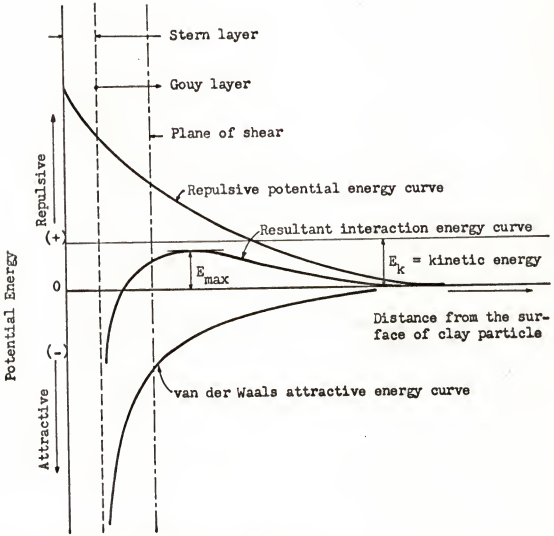


Fig. 10 - Potential Energy of Interaction.

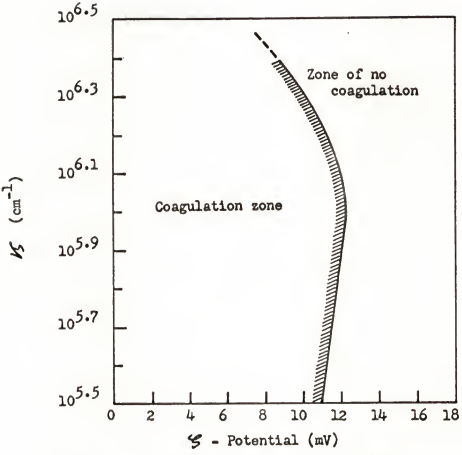


Fig. 11 - Critical Zeta Potential Curve. (From Tambo.[29]).

Flocculation

Definition. It is important that a distinction be made between the terms coagulation and flocculation to account for the different forces involved. According to La Mer flocculation should be defined as follows:[46] "We propose that the term flocculation should be restricted more in accordance with original usage corresponding to the Latin meaning of floc (L. flocculus - a small tuft of wool or a loosely fibrous structure). Flocculation is usually brought about by the action of high molecular weight materials (potato starch and polyelectrolytes in general) acting as linear polymers which bridge and unite the solid particles of the dispersion into a random structure which is three dimensional, loose, and porous."

Bridging Mechanism. Interparticle bridging action has been proposed by many investigators[49,50,51] as the basic mechanism in the flocculation of colloidal dispersions with polyelectrolytes. This same mechanism may also serve to explain the flocculation of clay suspensions with hydrolyzing metal coagulants. According to the bridging theory the polymer molecules are postulated to have part of themselves attached on the adsorption sites of the suspended particles and with other parts of the chains extended into the bulk of the solution. When these extended chain segments are adsorbed on the vacant adsorption sites of other suspended particles, bridges are established. Consequently, the particles are bound together and form small packets which can grow into big porous structural units until the shear gradient imposed by agitation in the system serves to prevent further growth.

Enmeshment Mechanism. The rapid flocculation of clay suspensions with aluminum salts has been explained by Packham[19] and Mackrle[24] as due to the physical enmeshment of the clay particles by the precipitation of the insoluble aluminum hydroxide. Under this enmeshment theory, it is postulated that the pH zone of optimum precipitation of aluminum hydroxide is the controlling factor in producing optimum flocculation.

Aluminum-Clay Interactions

The following experimental phenomena which take place in the interactions between aqueous aluminum ions and clay particles in dilute suspensions are believed to be most significant on the destabilization of the dilute clay suspensions.

Reduction of Zeta Potential

Depending upon the characteristics of the different types of counterions involved in the aluminum-clay-water systems, the repulsive zeta potential of the clays may be reduced in three different ways, as follows:

1. by the compression of the double-layer thickness in consequence of the incorporation of the simple cationic counterions into the diffuse Gouy double-layer;

2. by the specific adsorption of the cationic hydrolyzed species on the clay surface with a concurrent reduction in the surface potential of the clay particles; and

3. by the reduction of the particle surface charge, which is

accompanied by a reduction in the particle surface potential, as a result of the partial neutralization of particle charge by the attachment of aluminum hydroxides through physical enmeshment or mutual coagulation mechanism.

In general, the decrease in zeta potential is related to a decrease in the thickness of the electrical double-layer. The extent to which the double-layer thickness may be compressed depends upon the concentration and valence of the added counterions in the colloid system.

Adsorption

The aqua-complex ions of aluminum hydrolysis products may be adsorbed onto the adsorption sites of the clay particles by specific mechanisms. There are many types of adsorption models available for describing the various types of physical adsorptions.[48] Among those the Freundlich adsorption model is considered to best describe the case of the adsorption of the soluble aluminum hydrolysis products by kaolinite clay suspensions.

Adsorption Mechanisms. The adsorption process may be described by one or more of the following postulated mechanisms:

1. Hydrogen bonding between the clay and the counterion.

2. Adsorption through the agency of the residual valence forces in clay lattices.

3. A specific chemical reaction taking place on the surface of the clay between the adsorbed ion and the clay with the subsequent formation of an insoluble complex.

4. Dipole effect of the counterions.

Freundlich Adsorption Isotherm. The Freundlich adsorption isotherm equation may be written

$$\left(\frac{x}{m}\right) = KC^{1/n} \tag{14}$$

$$\text{or } \log\left(\frac{x}{m}\right) = \log K + \frac{1}{n}\log C \tag{15}$$

where x = weight of material adsorbed

m = weight of adsorbent

C = equilibrium concentration of the material being adsorbed

n,K = empirically derived constants

Charge Reversal

The phenomena of charge reversal of the clay particles in the coagulation of clay suspensions with metal ion coagulants, such as aluminum salts and ferric salts, have been demonstrated by many investigators.[14,26,28] The pH range of charge reversal generally corresponds to the range of the formation of the polynuclear hydrolysis products. Consequently, it has been postulated that the charge reversal is caused by the specific adsorption of a sufficient amount of the hydrolyzed polynuclear species onto the surface of colloids.[21] In addition to the above findings, a zone of redispersion of colloids has also been revealed to be consistent with the zone of charge reversal.

IV. EXPERIMENTAL MATERIALS AND PROCEDURES

Materials

Kaolinite Clay

The kaolinite clay used in preparing the clay suspensions in this investigation was the particular species, Kaolinite 4, supplied by Ward's National Science Establishment. This was the same clay used by Black and his coworkers in their previous coagulation studies.[14,26,51] The base exchange capacity of this clay is 8.7 milliequivalents per 100 grams, which was determined by Hannah using the ammonium acetate method.[52] In addition, the surface area of the kaolinite clay calculated from B.E.T. nitrogen gas adsorption data[53] was reported by Birkner to be 15.8 m^2/gm.

Aluminum Sulfate

The coagulant used in this study was reagent grade aluminum sulfate with a chemical formula $Al_2(SO_4)_3 \cdot 18H_2O$. The chemical analysis of this material is given in Table 4.

Reagents for pH Adjustment

Standardized 0.1 N HCl and 0.1 N NaOH solutions were used to adjust the final pH values of the clay suspensions.

Reagents for Aluminum Determination

The reagents used for determining the total aluminum are

Table 4

Analysis of Aluminum Sulfate*

Constituent	Per Cent by Weight
Assay $\left[Al_2(SO_4)_3 \cdot 18H_2O\right]$	103.0
Insoluble Matter	0.003
Chloride (Cl)	0.0008
Arsenic (As)	0.00003
Substances not Precipitated by NH_4OH (as SO_4)	0.10
Heavy Metals (as Pb)	0.0005
Iron (Fe)	0.0005
pH of 5% Solution at 25°C	2.4

*Analyzed by J. T. Baker Chemical Company, Phillipsburg, N. J.

described in the following sections:[54]

Standard 100 ppm Aluminum Solution. Dissolve 1.757 gm of aluminum potassium sulfate in distilled water containing 50 ml of 5 N hydrochloric acid and dilute to 1 liter.

1 Per Cent p-Nitrophenol. This indicator solution was obtained directly from W. H. Curtin and Company.

5 N Ammonium Hydroxide. Dilute 33 ml concentrated ammonium hydroxide to 100 ml with distilled water.

0.5 N Hydrochloric Acid. Dilute 4.5 ml of concentrated hydrochloric acid to 100 ml with distilled water.

1 Per Cent Thioglycollic Acid. The thioglycollic acid used was an analytical grade chemical supplied by Eastman Kodak Company.

Aluminon Reagent. Dissolve 0.25 gm of aluminon in 250 ml of distilled water, warming the solution. Add 5 gm of gum acacia followed by 87 gm of ammonium acetate and 126 ml of 5 N hydrochloric acid. Dilute to 500 ml and then filter under suction.

Procedures

Preparation of Kaolinite Clay Suspensions

Before it was suspended in demineralized water, the kaolinite clay was pulverized in a ball mill for a period of 24 hours and sieved through a 200 mesh screen, which has an average opening of 0.074 millimeter. One hundred twenty grams of the sieved kaolinite clay powder was suspended in 40 liters of demineralized water in a polyethylene carboy. The suspension was vigorously stirred for 12 hours with a high-speed mixer equipped with a long stainless steel shaft and propeller, after which the suspension was allowed to settle quiescently for 24 hours to separate the large size fractions. The supernatant portion of the settled clay suspension was then siphoned off and stored in another polyethylene carboy. The particle size of a clay suspension thus prepared will have a size range smaller than two microns as estimated from the Stokes law. Vigorous mixing was started two hours before and was continued through the entire process of pipetting various size aliquots of the settled clay suspension into individual 250 ml polyethylene bottles, which were then stoppered, labelled and stored until needed. When these different size

aliquots were diluted to two liters with demineralized water, the various values of clay concentration and initial clay turbidity as shown in Table 5 were obtained.

Table 5

Kaolinite Clay Suspensions

Clay Concentration* (mg/l)	Initial Turbidity (units)
15.8	20
18.8	24
31.7	41
37.2	51
47.5	67
61.5	102
63.3	104
73.9	125

*The clay concentrations were determined gravimetrically.

Preparation of Aluminum Sulfate Solutions

All aluminum sulfate solutions were prepared by dissolving an appropriate amount of reagent grade aluminum sulfate in demineralized water. Those solutions having concentration levels higher than 10 mg Alum/ml were prepared every two weeks, while those having concentrations lower than 10 mg Alum/ml were prepared at much shorter intervals, the

criterion being the maintenance of constant pH values, which were measured daily.

Alkalimetric Titrations

Standardization of 0.1 N Sodium Hydroxide Solution. The 0.1 N sodium hydroxide solution which was used for both alkalimetric titration and pH adjustment was precisely standardized by primary standard potassium acid phthalate solution, $KHC_8H_4O_4$.

Titration of Aluminum Sulfate Solution. Demineralized water was used to prepare the aluminum sulfate solutions for titration experiments. A Teflon-covered magnetic bar and a magnetic stirrer were used to mix the solution thoroughly for three minutes after the dropwise addition of the standardized 0.1 N sodium hydroxide solution. pH value of the solution was determined by the Beckman Model G pH Meter. The same procedure was repeated until a pH value of 10 was recorded. Through the entire titration process a pure nitrogen gas flow was bubbled through the solution being titrated. The temperature of the solution was maintained constant at 25°C.

Titration of Dilute Kaolinite Clay Suspension. The procedure for titrating the dilute kaolinite clay suspensions, which had different dosages of aluminum sulfate solution, with the standardized 0.1 N sodium hydroxide solution was similar to that used for the alum solutions.

Destabilization Experiments

The destabilization experiments which have been conducted in this investigation may be grouped into four different series as follows:

1. With the dosage of aluminum sulfate fixed at a selected constant value, but varying the final pH of the clay suspension.

2. With the final pH of the clay suspension fixed at a constant value of pH 3, but varying the dosage of aluminum sulfate. Four different clay concentrations were used.

3. With the final pH of the clay suspension fixed at a constant value of pH 5, but varying the dosage of aluminum sulfate. Four different clay concentrations were used.

4. With the final pH of the clay suspension fixed at a constant value of pH 8, but varying the dosage of aluminum sulfate. Four different clay concentrations were used.

Although there are some differences among the four series of experiments, the preparation of clay working suspension, function and intensity of agitation, sampling, residual turbidity measurements and pH measurements, as described in the following sections, were exactly the same in all series.

Preparation of Clay Working Suspensions. Six bottles of the kaolinite clay stock suspensions were used for each series of jar tests. The contents of the bottles were quantitatively transferred to separate two-liter volumetric flasks in which about one liter of the demineralized water had been placed. Appropriate amounts of 0.1 N HCl or 0.1 N NaOH were added to the flasks to yield the desired final pH values, and the flasks were then filled to the mark with additional demineralized water. A Teflon-covered magnetic bar was then placed in each flask and the flasks were then placed on magnetic stirrers. The suspensions were thoroughly

mixed for five minutes. One-liter graduated cylinders were then used to measure one liter of the suspension from each flask and this was transferred to a 48-oz square jar. The jars were placed on the multiple laboratory stirrer which was manufactured by Phipps and Bird, Inc. The suspensions remaining in the flasks were retained for the electrophoretic mobility determinations.

Function and Intensity of Agitation. The suspension in the 48-oz square jars was agitated by the stainless steel paddles on the multiple laboratory stirrer at a speed of 100 revolutions per minute for two minutes before and after the addition of appropriate dosages of aluminum sulfate. The speed was then reduced to 10 revolutions per minute for a period of 28 minutes. The suspensions were then allowed to settle quiescently for 10 minutes in order to separate the settleable flocs.

In addition, a second combination of mixing was used, which consisted of a 20-minute period of 100 rpm rapid mixing followed by a 10-minute period of 10 rpm slow mixing, followed by a period of 10-minute sedimentation. In all cases, a final pH of 5 was used.

Sampling. At the end of the prescribed sedimentation period 250 ml samples were withdrawn from each jar by an apparatus similar to that described by Cohen[55] at a level approximately one inch below the surface of the supernatant in the jar. The samples so obtained were used for residual turbidity and residual aluminum determinations.

Initial and Residual Turbidity Measurements. The initial and residual turbidities of the samples were measured with a Lumetron

Model 450 Filter Photometer.* The use of a 650 mμ red filter with a 75 mm light path in the cell was found to give sufficiently accurate readings of the turbidity values. The calibration of the Photometer was accomplished by comparing the optical density readings with the turbidity readings for each sample.[56] The optical density readings from the Photometer were plotted against the turbidity readings from a Jackson Candle Turbidimeter by the method described in Standard Methods.[57]

The initial turbidity of each clay suspension was determined by averaging the turbidity values of four samples of each suspension in which no coagulant or other reagent had been added.

In each destabilization experiment, the residual turbidity of each sample was measured promptly at the end of the sedimentation period.

pH Measurements. The destabilized suspensions which remained in the jars after the sampling process were used for the final pH determinations. All the pH determinations were made with a Beckman Model G pH Meter.**

Electrophoretic Mobility Determinations

Sample Preparation. Prior to the addition of the predetermined amount of aluminum sulfate, each of the remaining one-liter samples of

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*Manufactured by Photovolt Corp., New York, N. Y.

**Manufactured by Beckman Instruments, Inc., Fullerton, Calif.

the clay suspensions which were retained from the destabilization experiment was placed on a magnetic stirrer and mixed vigorously for five minutes. Mixing was continued for another five minutes after the dosing of aluminum sulfate, and then the electrophoretic mobility of the particles was immediately determined.

Measurements of Particle Electrophoretic Mobility. Throughout the entire course of this investigation, the Briggs microelectrophoresis cell was used to determine the electrophoretic mobilities of particles. The calibration of the cell as well as the procedure for determining particle mobilities were the same as those described and recommended in detail by Black and Smith.[58-60]

Specific Conductance Determinations. A Model IB-2A Impedance Bridge* with a pipette-form conductivity cell having a cell constant of 1 cm^{-1} was used for the measurements of the resistance of the clay suspensions. The specific conductance values were then calculated from these resistance data according to the procedure described in Standard Methods.[57]

pH Measurements. The pH of each sample was measured with a Beckman Model G pH Meter immediately after the mobility determination of the same sample was made

Calculation of Mobility Values. The electrophoretic mobilities of particles were calculated from the equation:[58]

---

*Manufactured by Heath Company, Benton Harbor, Michigan.

$$\mu = \frac{dX}{tIR_s} \qquad (16)$$

where μ = mobility, in μ/sec/v/cm

d = distance across a square of the Howard counter at a given magnification, in μ

X = cross sectional area of the cell, in cm^2

t = time for traveling across d, in seconds

I = current density, in amperes

R_s = specific resistance of the suspension, in ohm-centimeters

Determination of Residual Aluminum

Standard Curve Calibration. A standard curve was prepared on the Lumetron Model 450 Filter Photometer by using standards containing 0.0 to 1.5 mg/l aluminum, Al, prepared by dilution of the standard 100 ppm aluminum solution. A separate calibration curve was plotted for each new batch of aluminon reagent. The optical density readings of the standards were obtained by using a 530 mμ filter and a 3.75 mm light path in the cell.

Separation of Clay Particles. After the destabilization experiment was completed, a 250 ml sample of the supernatant was withdrawn from each jar as described in the previous section of sampling. A 100 ml of this sample was transferred into two 50-ml plastic centrifuge tubes, and then they were immediately centrifuged with a Model HR-1 International High-Speed Refrigerated Centrifuge* for 10 minutes at a speed

*Manufactured by International Equipment Company, Boston 35, Mass.

of 9,000 rpm to allow a complete separation of the clay particle from the liquid. The value of 9,000 rpm is equivalent to 4,600 x g.

Procedures for Aluminum Determinations. The procedures for determining the residual aluminum in the sample were basically the same as those developed by Packham.[54] The successive steps used in the aluminum determinations were as follows:

1. A 50 ml sample of the centrifugate, which was estimated to contain less than 0.075 mg of aluminum, was pipetted into a 100-ml volumetric flask. The volume of sample was reduced to 25 ml or 10 ml when the aluminum concentration was estimated to possibly exceed 0.075 mg, and a dilution factor was used to calculate the actual concentration of aluminum in the sample.

2. One drop of 1 per cent p-Nitrophenol indicator solution was added to the sample. Five N ammonium hydroxide was added drop by drop until the solution turned yellow.

3. The yellow coloration was then discharged by the dropwise addition of 0.5 N hydrochloric acid.

4. To the solution 16 drops of the freshly prepared 1 per cent thioglycollic acid and 10 ml of aluminon reagent was added. Demineralized water was then used to make up the volume to approximately 95 ml.

5. The flask was then immersed in boiling water for 20 minutes, after which it was removed from the boiling water and cooled rapidly in cold running water to around 20°C. Finally, the solution in the flask was made up to 100 ml with demineralized water.

6. The optical density values of the processed samples were

determined with the Lumetron Photometer, using a 530 mμ filter and a 3.75 mm light path in the cell.

Each jar test consisted of six individual experiments so that a total of six samples and one blank was prepared for every series of residual aluminum determinations.

Adsorption Computations

The difference between the total aluminum added to the clay suspension and the total aluminum still remaining in the centrifugate of the suspension was calculated and reported as the adsorption value.

Aluminum-Clay Kinetic Experiments

Aluminum Adsorption Rate. The adsorption rate of aluminum by kaolinite clay was determined by measuring the residual total aluminum in the centrifugate of the clay suspension at successive time intervals after the addition of a predetermined amount of aluminum. The adsorption values were computed in the same manner as that described in the previous section.

Duration and Intensity of Agitation. In order to evaluate the effects of the initial clay concentrations and the duration and intensity of agitation on the destabilization of the kaolinite clay suspensions at different pH values, the suspensions were mixed at a given intensity of agitation for a predetermined period of time, following which a period of 15 minutes was used to allow the destabilized suspensions to settle quiescently. Samples for residual turbidity determinations were then withdrawn by the same method as described in the previous section, and the determinations immediately made.

V. RESULTS AND DISCUSSION

Variable pH Series

The series of studies in which the pH value is varied was performed using two different approaches. In the first, the destabilization experiments were performed on kaolinite clay suspensions which had the same clay concentration value of 61.5 mg/l. The final pH of the destabilized suspensions was varied from 3 to 10, while the dosages of aluminum sulfate used were 3, 5, 7, 10, 15, 20, 30 and 50 mg/l. The experimental results of this part of the study are shown in Figures 12 to 19.

In the second approach, the experiments were conducted using kaolinite clay suspensions having three different initial clay concentrations and in the neutral to slightly alkaline pH range of from pH 6 to 8 with dosages of 5, 10, 30 and 50 mg/l of aluminum sulfate. Figures 22 to 25 show the results obtained for the second series.

Role of pH on Aluminum Sorption

The aluminum sorption curves as depicted in Figures 12 to 19 reveal several significant phenomena which are discussed in the following sections:

1. Only a small fraction of the aluminum ions was adsorbed on kaolinite clay particles at pH values below pH 4 and above pH 9, and practically no sorption of aluminum ions by the clay particles was

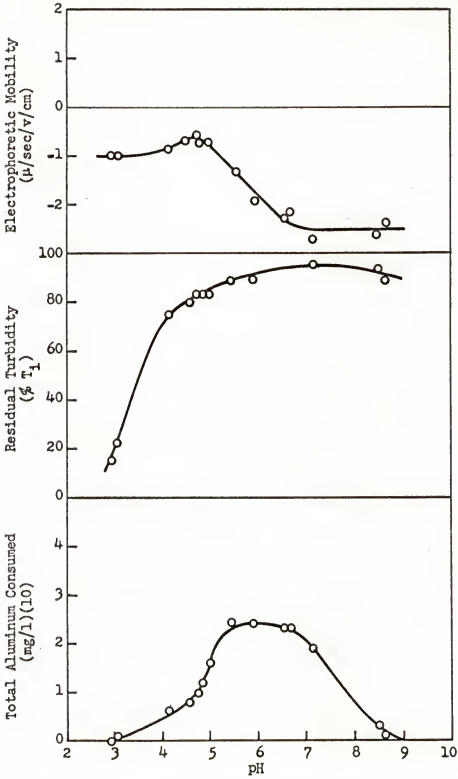

Fig. 12 - The Effect of pH on the Destabilization of Kaolinite Clay Suspension. Aluminum Sulfate Dosage = 3 mg/l. Clay Concentration = 61.5 mg/l.

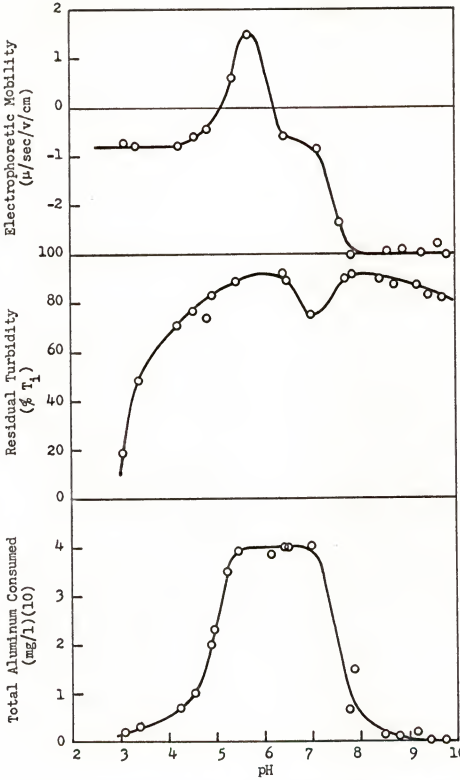

Fig. 13 - The Effect of pH on the Destabilization of Kaolinite Clay Suspension. Aluminum Sulfate Dosage = 5 mg/l. Clay Concentration = 61.5 mg/l.

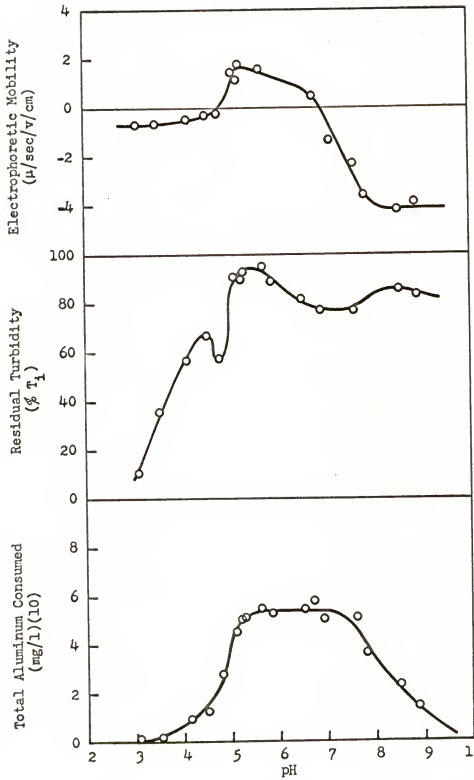

Fig. 14 - The Effect of pH on the Destabilization of Kaolinite Clay Suspension. Aluminum Sulfate Dosage = 7 mg/l. Clay Concentration = 61.5 mg/l.

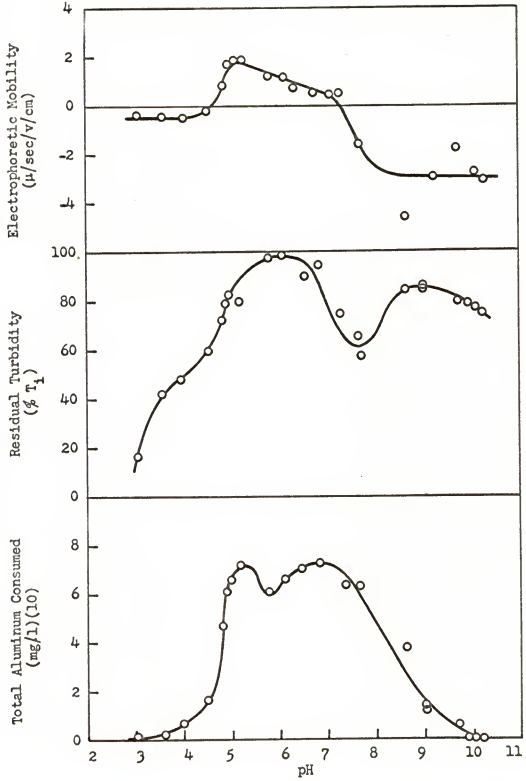

Fig. 15 - The Effect of pH on the Destabilization of Kaolinite Clay Suspension. Aluminum Sulfate Dosage = 10 mg/l. Clay Concentration = 61.5 mg/l .

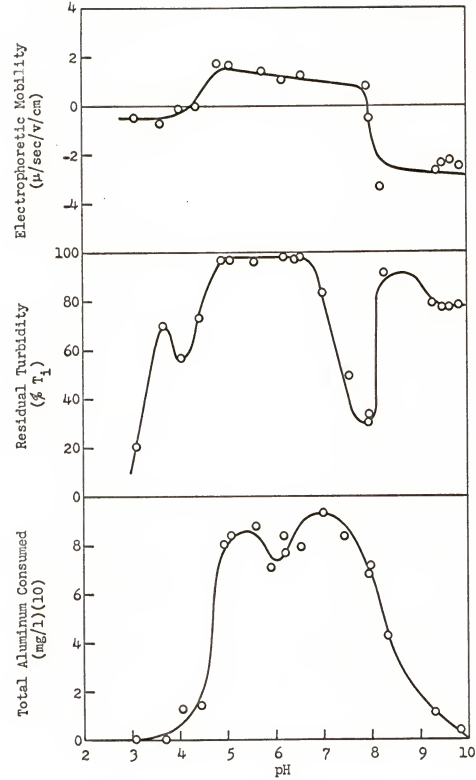

Fig. 16 - The Effect of pH on the Destabilization of Kaolinite Clay Suspension. Aluminum Sulfate Dosage = 15 mg/l. Clay Concentration = 61.5 mg/l.

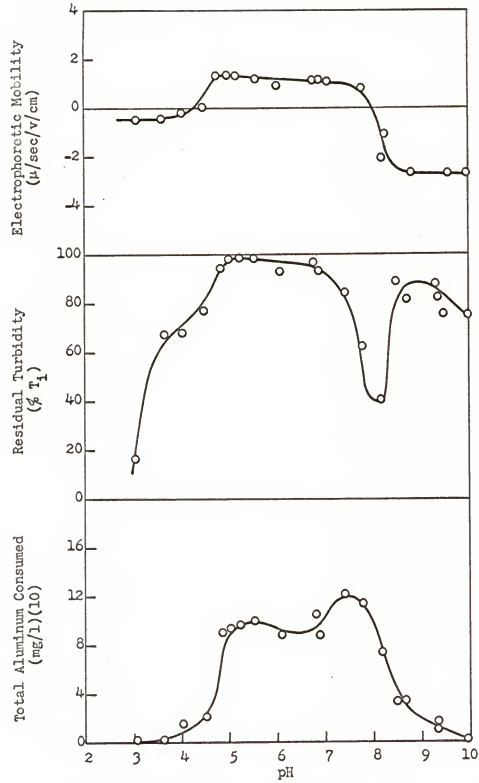

Fig. 17 - The Effect of pH on the Destabilization of Kaolinite Clay Suspension. Aluminum Sulfate Dosage = 20 mg/l. Clay Concentration = 61.5 mg/l.

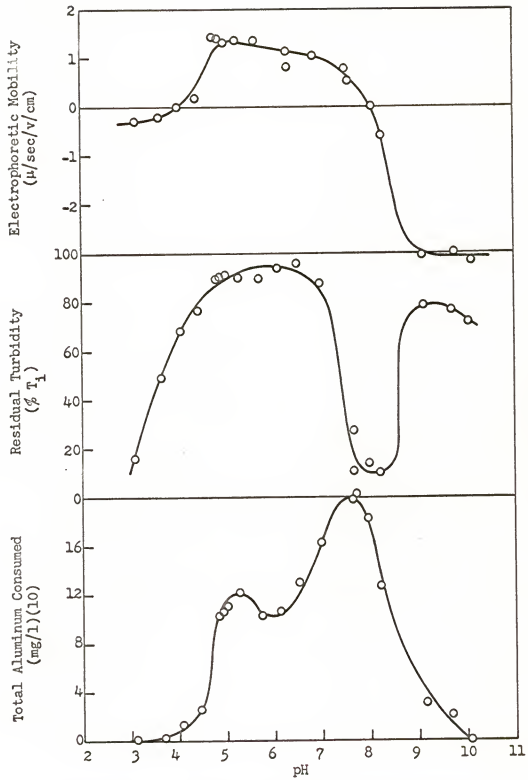

Fig. 18 - The Effect of pH on the Destabilization of Kaolinite Clay Suspension. Aluminum Sulfate Dosage = 30 mg/l. Clay Concentration = 61.5 mg/l.

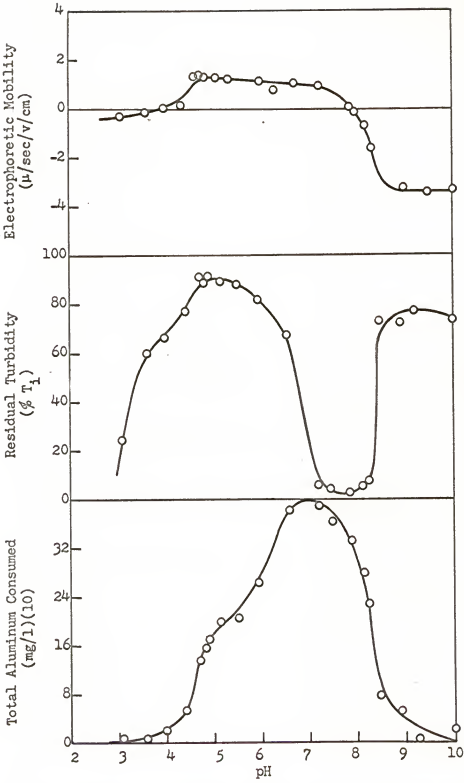

Fig. 19 - The Effect of pH on the Destabilization of Kaolinite Clay Suspension. Aluminum Sulfate Dosage = 50 mg/l. Clay Concentration = 61.5 mg/l.

observed at pH 3 and pH 10. These data are believed to support the hypotheses[21] that the predominant species at pH values below pH 4 is the simple trivalent aluminum ion, Al^{+++}, while in the alkaline pH range aluminum is present mainly as the negatively charged aluminate ion, $Al(OH)_4^-$. It would appear that these two species are not strongly adsorbed by the clay particles.

2. In the range from pH 4 to pH 9, two peaks were found on the aluminum sorption curves when intermediate dosages of aluminum sulfate were used. The pH value of the first peak at the lower pH values is found to correspond very well to the equilibrium pH at which 99 per cent of the added aluminum ions is present as $Al_6(OH)_{15}^{+++}$ as proposed by Brosset and his coworkers.[32] The second peak of the aluminum sorption curve on the higher pH side is believed to represent the pH value at which maximum precipitation of aluminum hydroxide occurs. A comparison between the calculated and observed values for four different dosages is shown in Table 6.

A series of aluminum adsorption isotherms based on the interpolated data from Figures 12 to 19 is shown in Figure 20. The Freundlich adsorption isotherm plots of these data at three selected pH values are shown in Figure 21.

Relationship Between Mobility and Residual Turbidity

The relationships between the electrophoretic mobility values and residual turbidity shown in Figures 12 to 19 are not so readily defined and correlated. However, there are several interesting and

Table 6

Comparison of pH Values for Maximum Hydrolysis and Maximum Adsorption of Aluminum Ion

Dosage of Aluminum Sulfate (mg/l)	Equilibrium pH at Which $\frac{6\,[Al_6(OH)_{15}^{+++}]}{[Al_T]} = 99\%$	Experimental pH for Maximum Aluminum Adsorption in Acid pH Range	Discrepancy Between the two pH Values
3	5.57	--	--
5	5.49	--	--
7	5.45	--	--
10	5.39	5.25	-0.14
15	5.35	5.35	0.00
20	5.29	5.35	0.06
30	5.23	5.25	0.02
50	5.16	--	--

significant conclusions which may be drawn from them. Among them the most important are the following:

1. At pH values below pH 4, the electrophoretic mobilities of the clay particles gradually become more positive with increasing alum dosages. This change identified a zone of fair to good turbidity removal, termed by Langelier and Ludwig, who first observed it, peri-kinetic or electrokinetic coagulation.

2. The first isoelectric point appeared in the pH range from 4 to 5. This isoelectric pH value decreased with an increase in the

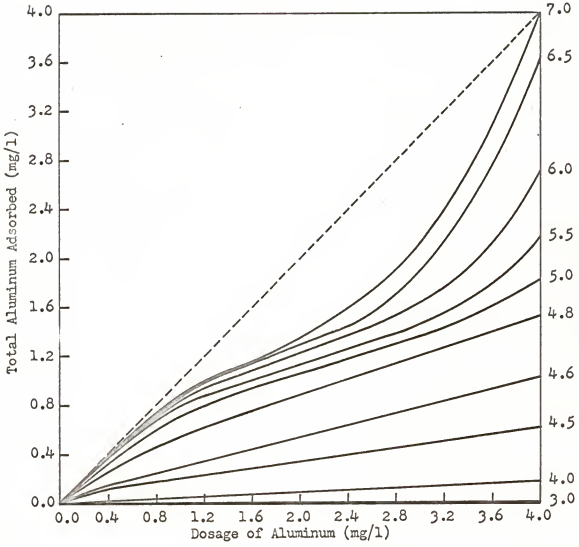

Fig. 20 - The Effect of pH on the Adsorption Isotherms. Kaolinite Clay Concentration = 61.5 mg/l. (The figures on the right side are pH values).

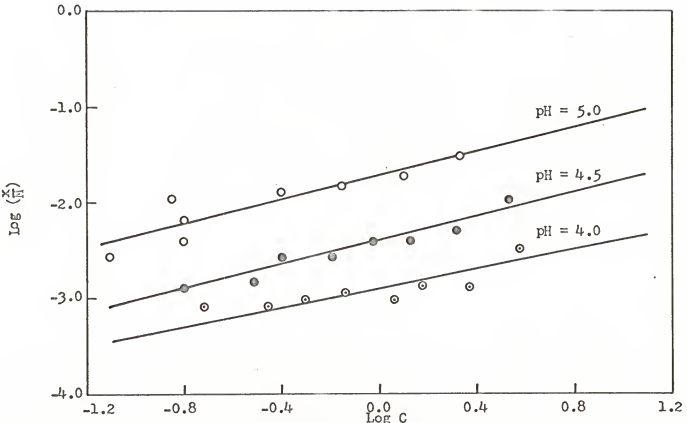

Fig. 21 - The Effect of pH on the Freundlich Adsorption Isotherms of Kaolinite Clay Suspensions. Kaolinite Clay Concentration = 61.5 mg/l.

dosage of aluminum sulfate. The second isoelectric point appeared in the range from pH 6 to pH 8, the pH value increasing with increasing alum dosage. Therefore, the charge reversal zone falling between the two isoelectric pH values was broadened with an increase in the dosage of aluminum sulfate. In addition, the first isoelectric pH, when the mobility changed from negative to positive, marked the beginning of a redispersion zone essentially identical with the zone of charge reversal, first pointed out by Black and Hannah.[14] The second isoelectric pH at which the mobility changed from positive to negative identified the beginning of a pH zone of optimum turbidity removal.

3. The maximum charge reversal was generally accompanied by maximum redispersion. Moreover, the pH value of the maximum charge reversal was slightly decreased from 5.7 to 4.9 with an increase in the aluminum sulfate dosage from 3 mg/l to 50 mg/l.

Effect of Initial Clay Concentration on Destabilization

The data shown in Figures 22 to 25 were mostly obtained within pH range from 6 to 8 within which the aluminum hydroxide has been supposed to be the most predominant aluminum species. Those curves showed that when the dosages of aluminum sulfate were less than 30 mg/l the initial clay concentration had an influence on all of the clay mobility, the residual turbidity and the total aluminum consumption measurements. Clay suspensions with higher concentration of clay particles were more readily destabilized than those with lower clay concentrations. However, when a high dosage of aluminum sulfate, specifically 50 mg/l was used, the initial clay concentration had practically

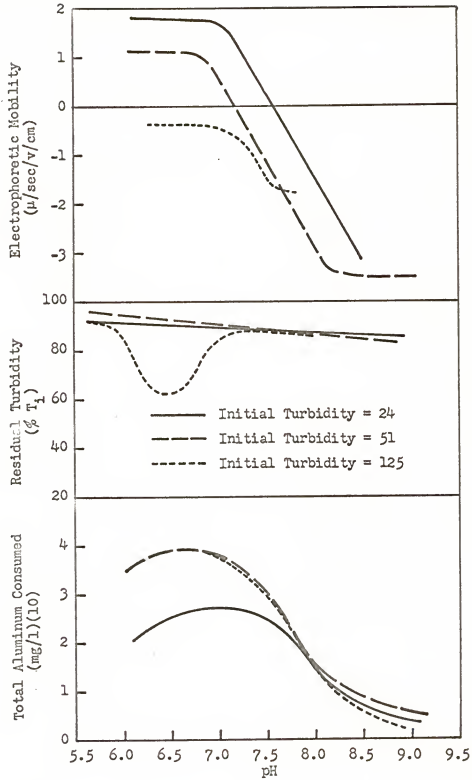

Fig. 22 - The Effect of Initial Clay Concentration on the Destabilization of Kaolinite Clay Suspensions with Aluminum Sulfate. Aluminum Sulfate Dosage = 5 mg/l.

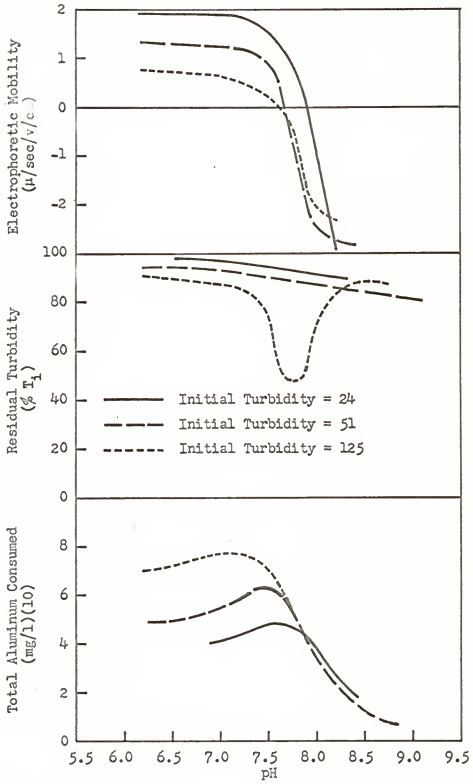

Fig. 23 - The Effect of Initial Clay Concentration on the Destabilization of Kaolinite Clay Suspensions with Aluminum Sulfate. Aluminum Sulfate Dosage = 10 mg/l.

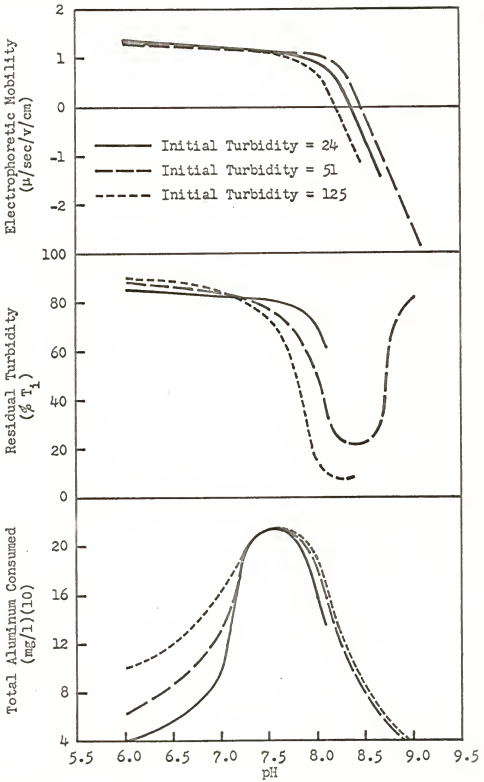

Fig. 24 - The Effect of Initial Clay Concentration on the Destabilization of Kaolinite Clay Suspensions with Aluminum Sulfate. Aluminum Sulfate Dosage = 30 mg/l.

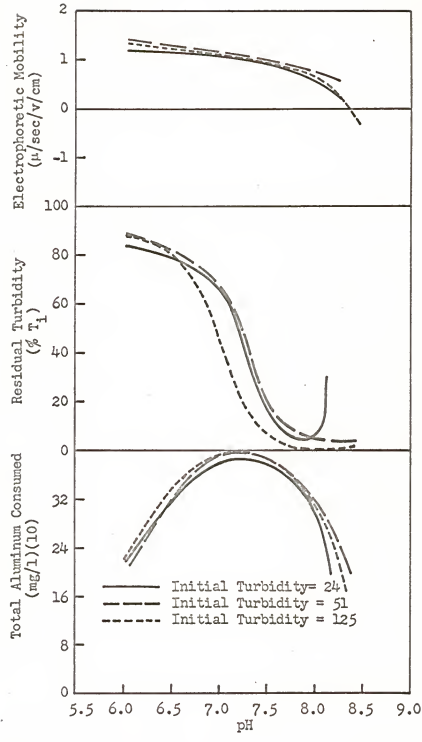

Fig. 25 - The Effect of Initial Clay Concentration on the Destabilization of Kaolinite Clay Suspensions with Aluminum Sulfate. Aluminum Sulfate Dosage = 50 mg/l.

no effect on the values of the three determinations. In addition, the aluminum consumption curves reveal that all three clay concentration curves are quite similar in the pH range above pH 7.5.

The simple physical enmeshment mechanism as proposed by Packham to describe the coagulation of the dilute clay suspensions with aluminum salts[19] is applicable only in those systems in which the concentrations of the applied aluminum ion are sufficiently high so that abundant amount of aluminum hydroxide flocs can be rapidly formed to sweep down the suspending clay particles. However, for low alum dosages, mutual coagulation as proposed earlier by Black[61] would appear to be better mechanism for describing the destabilization of dilute clay suspensions with aluminum salts in the neutral pH range.

When a clay suspension can be destabilized by the physical enmeshment mechanism, the concentration of clay particles may have very little effect. However, the clay concentration becomes a critical factor when mutual coagulation is the controlling mechanism of the destabilization process. The experimental results shown in Figure 25, using 50 mg/l aluminum sulfate dosage, support the assumption of the validity of a physical enmeshment mechanism, while the results in Figures 22 to 24, using aluminum sulfate dosages less than 30 mg/l, can be better understood by assuming mutual coagulation as the mechanism of destabilization.

Log [Al] vs. pH

The destabilization of a dilute clay suspension with aluminum salts is largely controlled by the hydrolytic reactions of the aluminum

ions, which in turn are functions of the pH and the concentration of aluminum ions present in the system. Consequently, a more comprehensive understanding of the destabilization of a clay suspension may be achieved through a study of the log [Al] - pH plot in which the various regions of coagulation and flocculation are very well defined by both pH value and the logarithm of the molar concentration of aluminum. The experimental results of the variable pH series of this study are summarized and plotted in the form of log [Al] - pH as shown in Figure 26.

Constant pH Series

In the constant pH series, three different final pH values, namely, pH 3, pH 5 and pH 8, were chosen for investigation in an attempt to elucidate the various mechanisms involved in the destabilization processes in those pH ranges within which the existence of different predominant aluminum ion species have been proposed.[21,32] The trivalent metallic aluminum ion, Al^{+++}, is the main species in the region below pH 4. In the range between pH 4 and pH 6, the formation of hydrolyzed polynuclear complexes, such as $Al_6(OH)_{15}^{+++}$ or $Al_8(OH)_{20}^{++++}$, has been proposed. In the neutral pH zone from pH 6 to pH 8, insoluble aluminum hydroxide, $Al(OH)_3$, or colloidal basic salts are believed to be the principal species present.

Destabilization at Constant pH 3

The results of this series of experiments are shown in Figures 27 to 30. The curves of particle electrophoretic mobility and aluminum adsorption are quite similar for the four clay suspensions which had

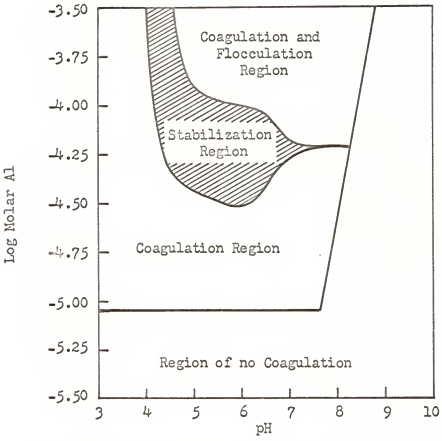

Fig. 26 - The Entire Log (Al) - pH Domain for a Kaolinite Clay Suspension. Clay Concentration = 61.5 mg/l.

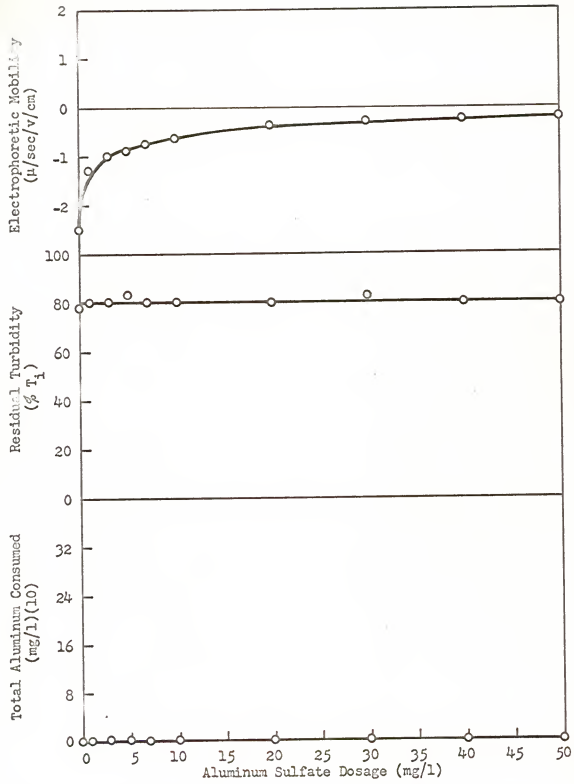

Fig. 27 - The Destabilization of a Kaolinite Clay Suspension with Aluminum Sulfate. Initial Clay Concentration = 15.8 mg/l. Final pH of Suspension = 3.0.

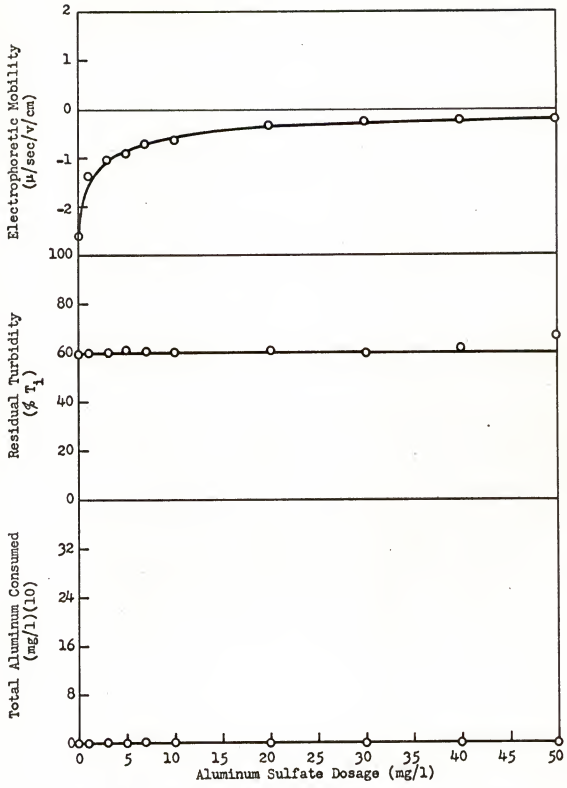

Fig. 28 - The Destabilization of a Kaolinite Clay Suspension with Aluminum Sulfate. Initial Clay Concentration = 31.7 mg/l. Final pH of Suspension = 3.0.

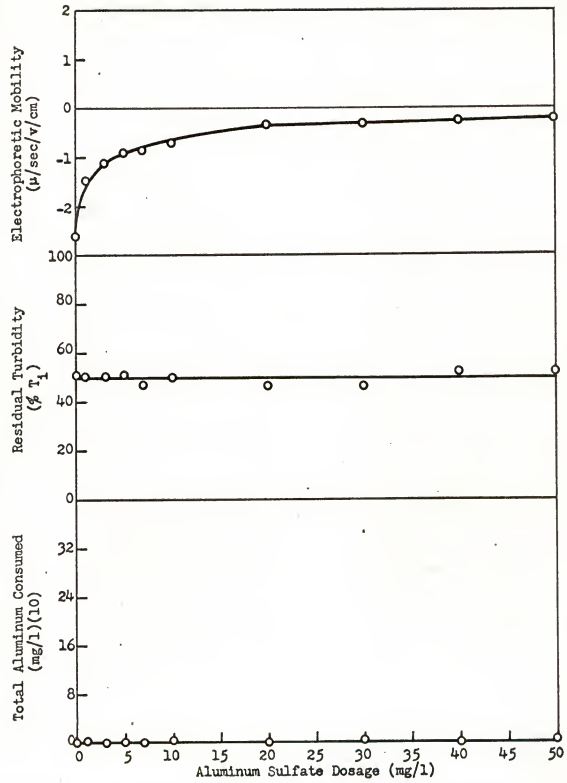

Fig. 29 - The Destabilization of a Kaolinite Clay Suspension with Aluminum Sulfate. Initial Clay Concentration = 47.5 mg/l. Final pH of Suspension = 3.0.

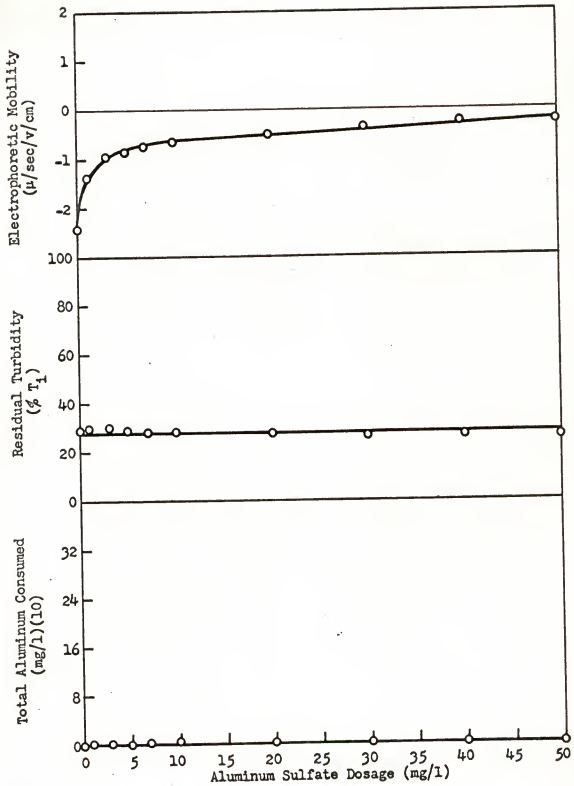

Fig. 30 - The Destabilization of a Kaolinite Clay Suspension with Aluminum Sulfate. Initial Clay Concentration = 63.3 mg/l. Final pH of Suspension = 3.0.

different initial clay concentrations, namely, 15.8, 31.7, 47.5 and 63.3 mg/l. When the residual turbidity is expressed as per cent of the initial clay turbidity, the clay suspension which had the highest clay concentration was found to have the lowest residual turbidity.

The addition of aluminum sulfate in dosages from 5 mg/l up to 50 mg/l had no effect upon either the residual turbidity or the adsorption of aluminum ions for any one of the four clay suspensions. However, increasing the dosage of aluminum sulfate decreased the negative mobility of the floc particles at all dosages employed from -2.5 μ/sec/v/cm to about -0.3 μ/sec/v/cm.

According to Matijevic[21] the hydrated trivalent metallic aluminum ion does not reverse the charge of negative silver halide sols, and this same behavior has been shown to take place in the kaolinite clay suspensions, as revealed in Figures 27 to 30. Also, no adsorption of the trivalent Al^{+++} ion was found at this pH value throughout the entire range of dosages employed.

The reduction in the negative mobility of the clay particles by an increase in aluminum ion concentration is believed to be brought about by the reduction of the double-layer thickness of the clay particle in consequence of an increase of the ionic strength in the suspension system. Therefore, the behavior of the trivalent metallic aluminum ions in the clay colloidal systems is simply to intensify the ionic atmosphere surrounding every clay particle to compress the double-layer of the particle with a reduction in the double-layer thickness. As a result of this reduction in the thickness of the double-layer

surrounding a clay particle, the zeta potential of the clay particle is reduced, as shown by much lower negative mobility values.

Although the electrophoretic mobility curves in all four clay suspensions investigated are almost identical, the percentages of initial turbidity remaining after coagulation were not the same, and the curves show an inverse relationship between concentration and final turbidity. These differences in residual turbidity at different initial clay concentrations may be explained by the Smoluchowski theory[62] which is based upon the probability factor in particle collisions during the process of coagulation. According to this theory, where all variables except clay concentration are held constant, the suspension which has higher initial clay concentration should be easier to destabilize with a greater reduction in clay turbidity.

Destabilization at Constant pH 5

Figures 31 to 34 show the results of the series of experiments in which the final pH values were maintained at constant pH 5. The predominant species at this pH value is believed to be either the polynuclear complex, $Al_6(OH)_{15}^{+++}$ or $Al_8(OH)_{20}^{++++}$, as proposed by Brosset[32] and Matijevic[21] respectively.

Two types of agitation were used to bring about destabilization in this series. The first type was two minutes of rapid mixing at 100 rpm followed by a period of 28 minutes of slow mixing at a speed of 10 rpm, followed by a 10 minute sedimentation period. The results for this series are shown in the solid line curves in Figures 31 to 34. The second type employed 20 minutes of rapid mixing at 100 rpm followed

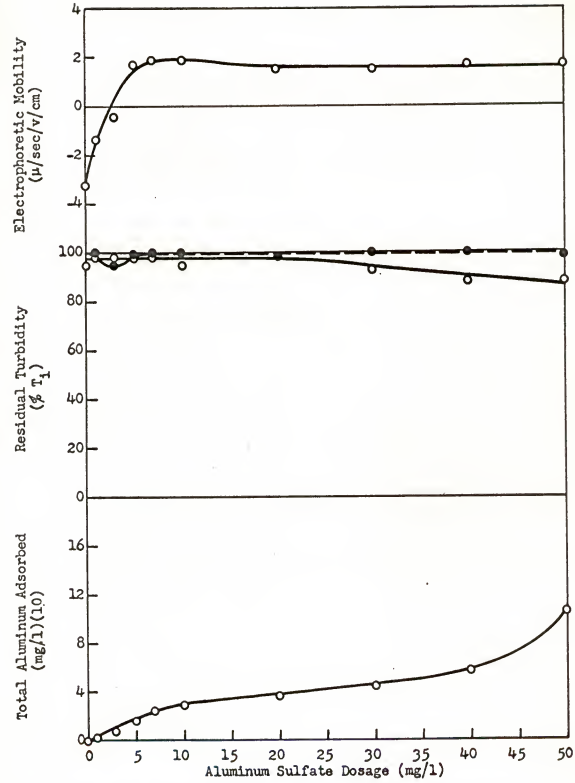

Fig. 31 - The Destabilization of a Kaolinite Clay Suspension with Aluminum Sulfate. Initial Clay Concentration = 15.8 mg/l. Final pH of Suspension = 5.0 ± 0.05.

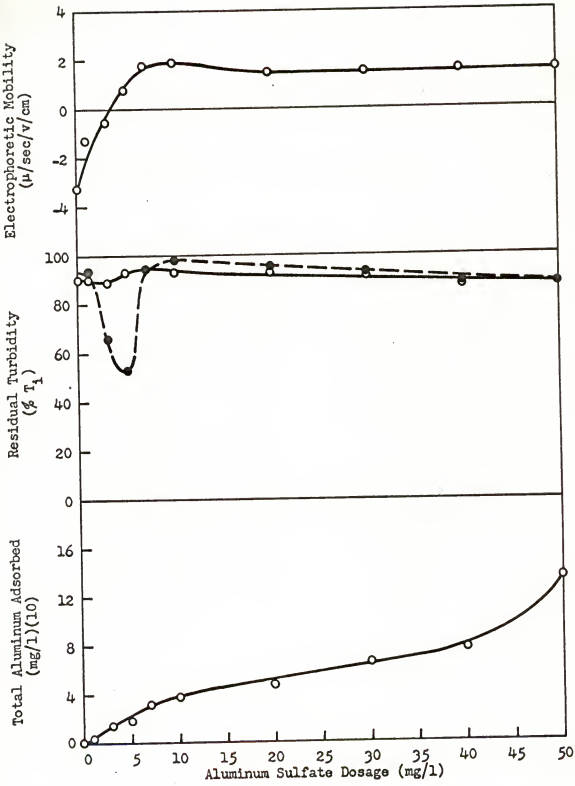

Fig. 32 - The Destabilization of a Kaolinite Clay Suspension with Aluminum Sulfate. Initial Clay Concentration = 31.7 mg/l. Final pH of Suspension = 5.0 ± 0.05.

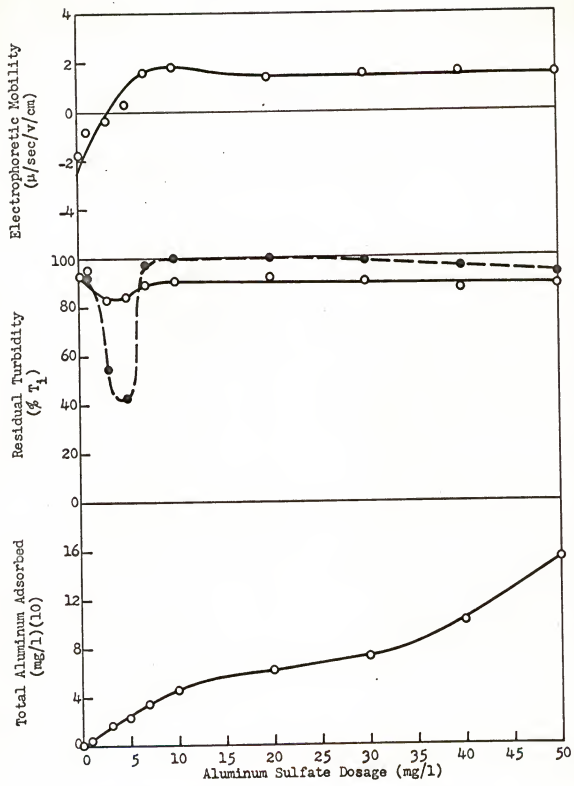

Fig. 33 - The Destabilization of a Kaolinite Clay Suspension with Aluminum Sulfate. Initial Clay Concentration = 47.5 mg/l. Final pH of Suspension = 5.0 ± 0.05.

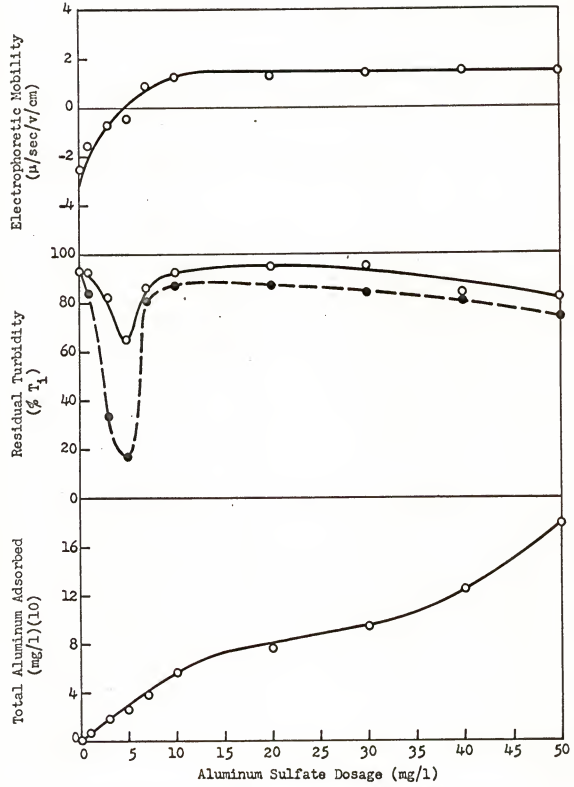

Fig. 34 - The Destabilization of a Kaolinite Clay Suspension with Aluminum Sulfate. Initial Clay Concentration = 63.3 mg/l. Final pH of Suspension = 5.0 ± 0.05.

by a period of 10 minutes of slow mixing and 10 minutes sedimentation. The dash line curves in Figures 31 to 34 show the experimental results obtained with this type of mixing. The second type of mixing provides more kinetic energy for the particles and thus results in better turbidity removal. The differences in the percentage of the initial turbidity remaining after coagulation at different initial clay concentrations may, as before, be accounted for in terms of Smoluchowski's theory.

The electrophoretic mobility curves show that the aluminum hydrolysis products formed at this pH value are capable of reversing the originally negative charge of the clay particles. These charge reversal phenomena, which occurred in the case of all of the four suspensions, support the theory proposed by Matijevic,[21] and much earlier, by Mattson,[8] that the hydrolyzed aluminum species are able to reverse the charge of the negatively charged sols. The mechanism for this charge reversal may be the over-neutralization of the surface charge of the clay particle by the strongly adsorbed multivalent hydrolyzed aluminum species in consequence of a specific adsorption of the hydrolyzed aluminum ions by the ions on the clay surface.

A very narrow zone of coagulation appears at the point where the mobility values change from negative to positive. Beyond this point, the clay suspension was again stabilized. This same phenomenon was fully demonstrated by Black and his associates[51] in their studies of the destabilization of dilute clay suspensions with labelled polymers. Consequently, the polymerization tendency of the aluminum hydroxo

complexes as proposed by Stumm and Morgan[25] can be indirectly supported by the present experimental results. Figure 35 summarizes the effect of the initial clay concentration on the destabilization of kaolinite clay suspensions with aluminum sulfate at pH 5.

The aluminum adsorption data shown in Figures 31 to 34 may also be plotted as Freundlich adsorption isotherms. Figures 36 to 39 show the plots of these Freundlich adsorption isotherms. Figure 40 shows the effect of the initial clay concentration on the Freundlich adsorption isotherm. The concave inflection at the right ends of the adsorption curves as shown in Figures 31 to 34 may be due to the presence of colloidal aluminum hydroxides which can be removed by centrifuge separation since, as shown in Figure 41, 12 per cent of the aluminum added was removed by centrifuging.

The empirical constants of the Freundlich adsorption isotherm equation for each of the four clay suspensions investigated were calculated, using the sample linear regression equation,[63] and the calculated results are shown in Table 7.

Destabilization at Constant pH 8

The experiments in this series were performed using four different kaolinite clay suspension concentrations, varying from 15.8 mg/l to 63.3 mg/l. Figures 42 to 45 show the individual results for each of the four clay suspensions investigated. A summary of these is shown in Figure 46.

It is clearly demonstrated that the aluminum consumption curves are only slightly influenced by the difference in initial clay

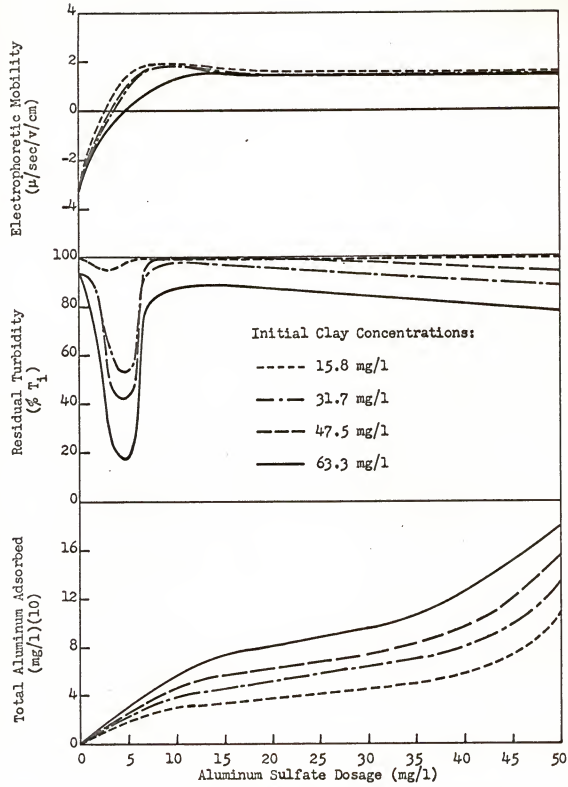

Fig. 35 - The Effect of Initial Clay Concentration on the Destabilization of Kaolinite Clay Suspensions with Aluminum Sulfate. Final pH of Suspensions = 5.0 ± 0.05.

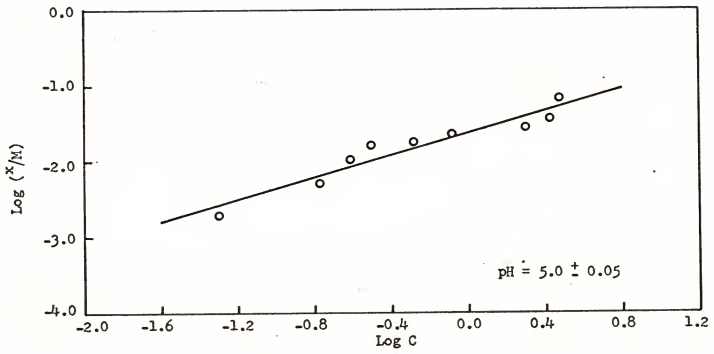

Fig. 36 - Freundlich Adsorption Isotherm. Kaolinite Clay Concentration = 15.8 mg/l.

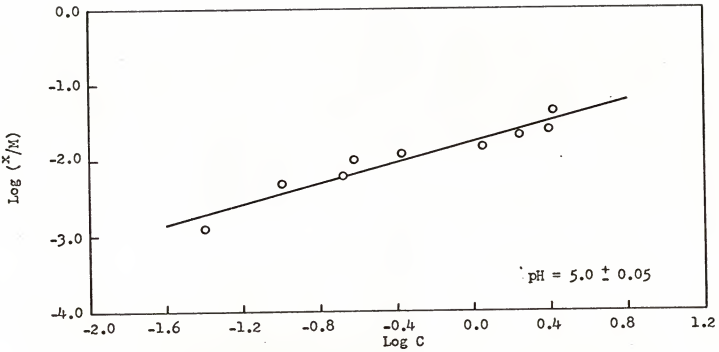

Fig. 37 - Freundlich Adsorption Isotherm. Kaolinite Clay Concentration = 31.7 mg/l.

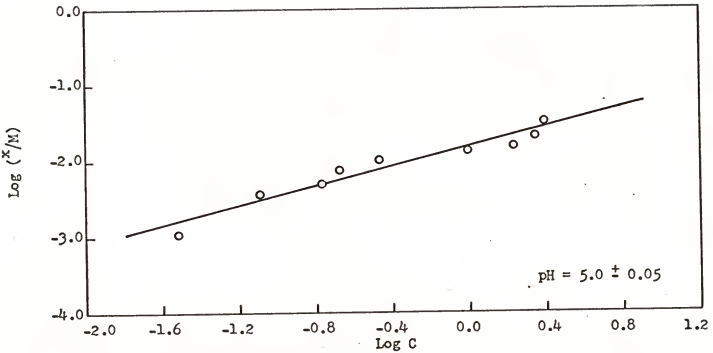

Fig. 38 - Freundlich Adsorption Isotherm. Kaolinite Clay Concentration = 47.5 mg/l.

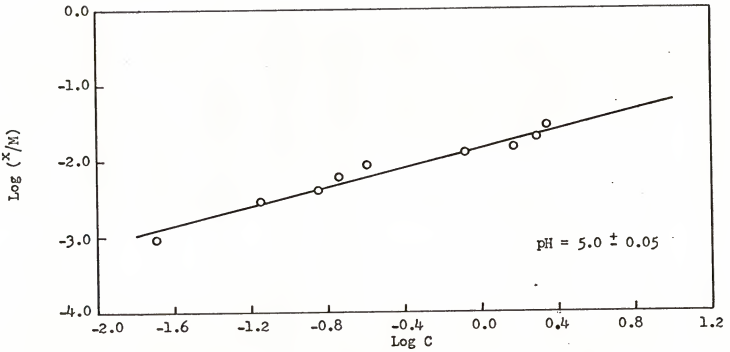

Fig. 39 - Freundlich Adsorption Isotherm. Kaolinite Clay Concentration = 63.3 mg/l.

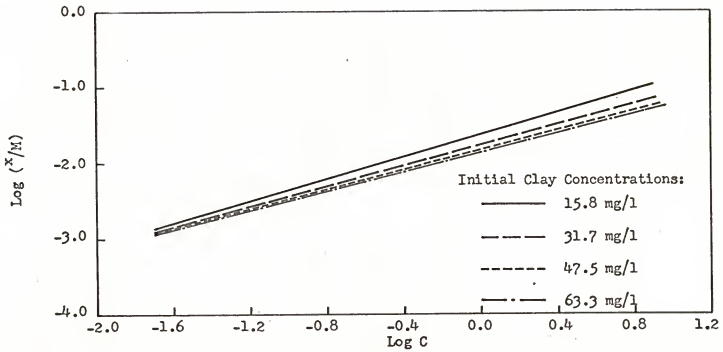

Fig. 40 - The Effect of Initial Clay Concentration on the Freundlich Adsorption Isotherms of Aluminum-Kaolinite Systems. pH = 5.0 ± 0.05.

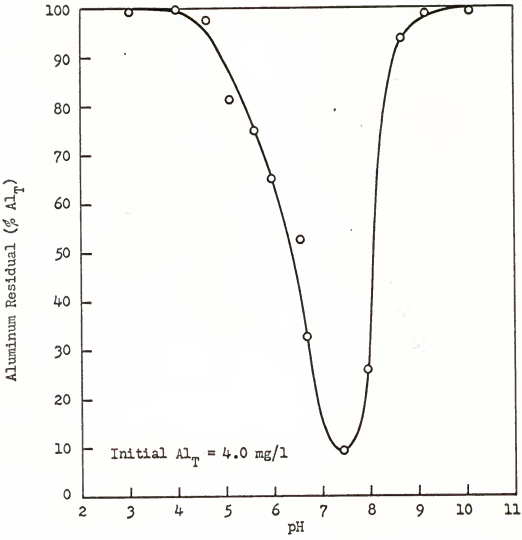

Fig. 41 - The Effect of pH on Aluminum Residual After Separation by High-Speed Centrifuge.

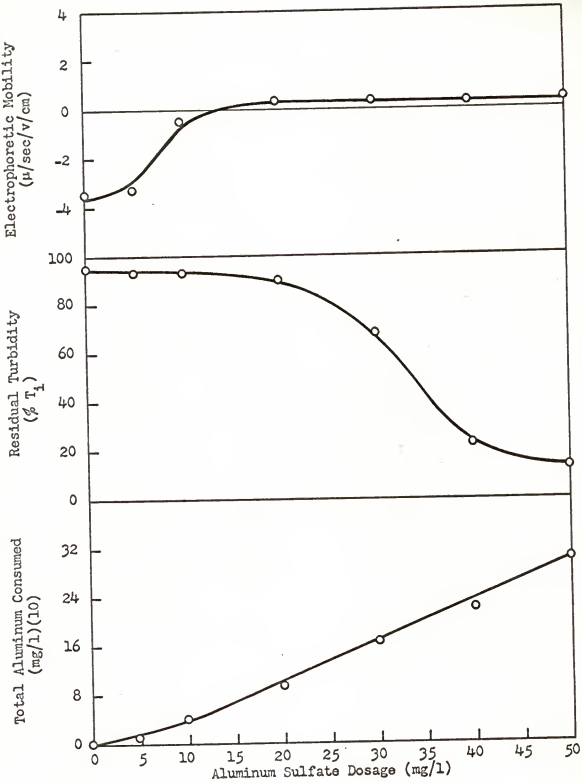

Fig. 42 - The Destabilization of a Kaolinite Clay Suspension with Aluminum Sulfate. Initial Clay Concentration = 15.8 mg/l. Final pH of Suspension = 8 ± 0.1.

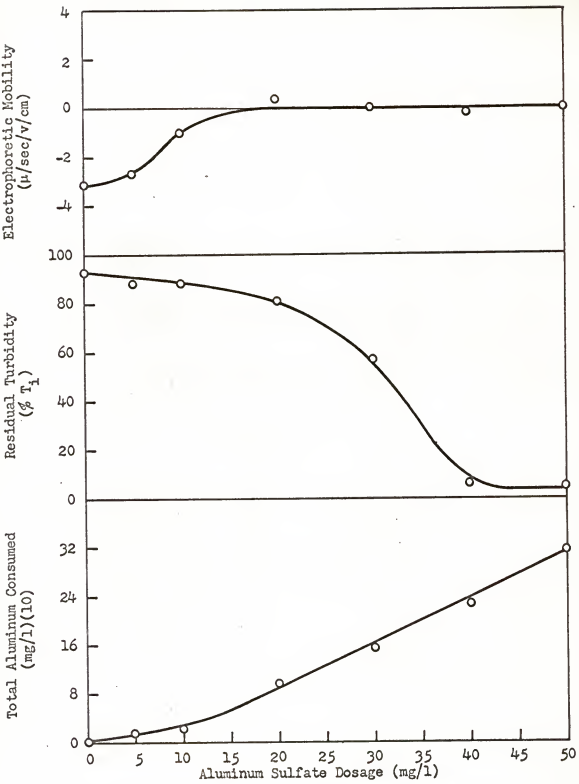

Fig. 43 - The Destabilization of a Kaolinite Clay Suspension with Aluminum Sulfate. Initial Clay Concentration = 31.7 mg/l. Final pH of Suspension = 8 $\pm$ 0.1.

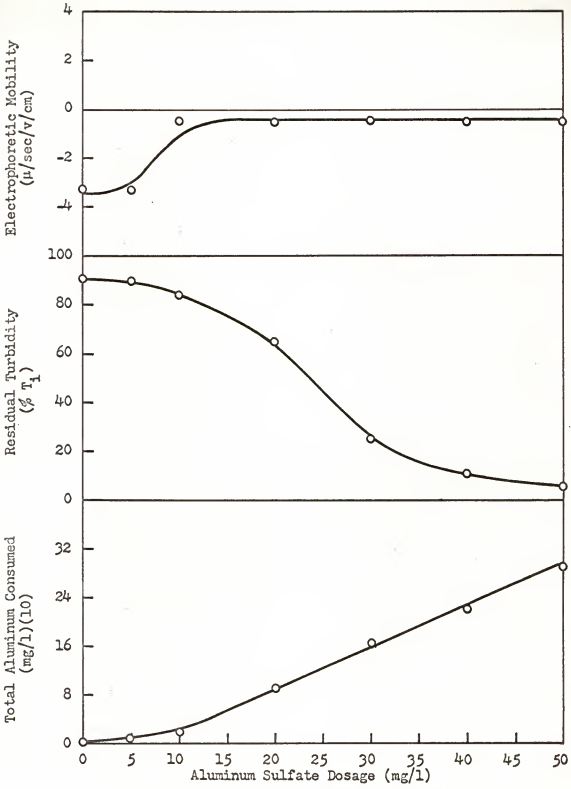

Fig. 44 - The Destabilization of a Kaolinite Clay Suspension with Aluminum Sulfate. Initial Clay Concentration = 47.5 mg/l. Final pH of Suspension = 8 ± 0.1.

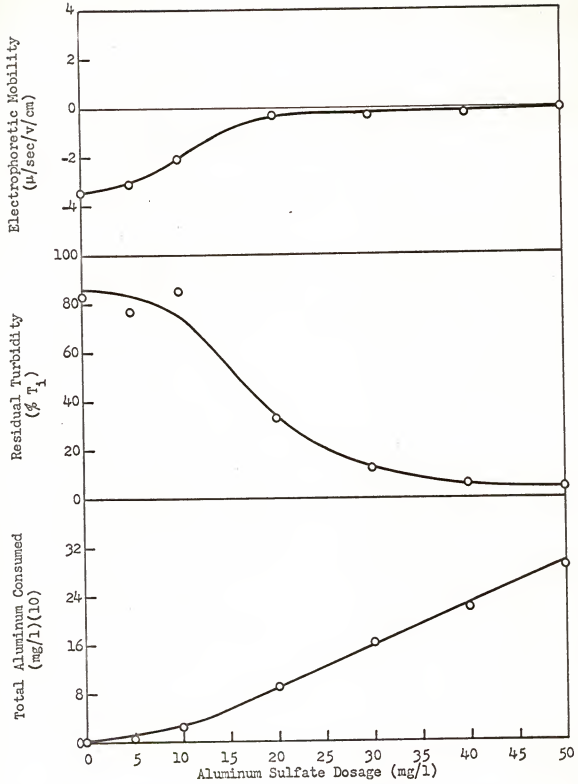

Fig. 45 - The Destabilization of a Kaolinite Clay Suspension with Aluminum Sulfate. Initial Clay Suspension = 63.3 mg/l. Final pH of Suspension = 8 ± 0.1.

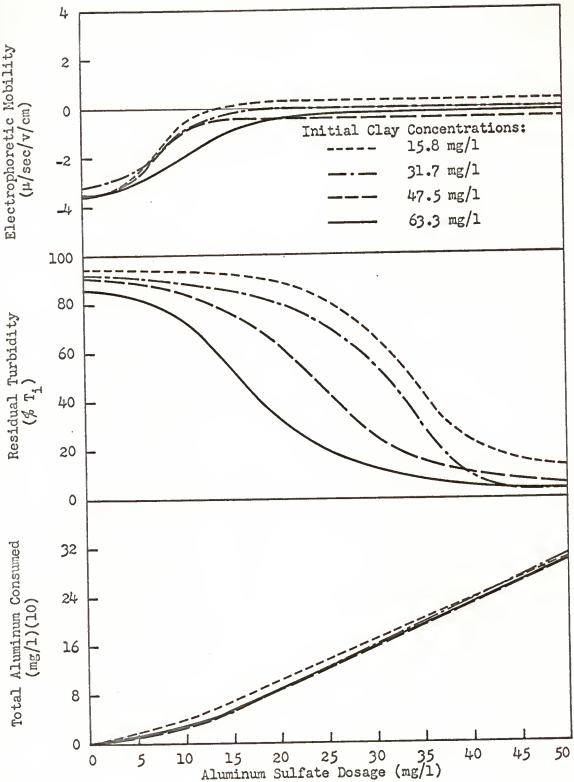

Fig. 46 - The Effect of Initial Clay Concentration on the Destabilization of Kaolinite Clay Suspensions with Aluminum Sulfate. Final pH of Suspensions = 8 ± 0.1.

Table 7

The Empirical Constants of the Freundlich Adsorption Isotherm Equation*

Kaolinite Clay Concentration (mg/l)	log K	K x (10)^2	$\frac{1}{n}$	n
15.8	-1.64	2.29	0.73	1.37
31.7	-1.76	1.74	0.68	1.47
47.5	-1.82	1.51	0.65	1.54
63.3	-1.84	1.45	0.63	1.59

*The form of the Freundlich isotherm used is

$$\log \frac{X}{M} = (\frac{1}{n}) \log C + \log K$$

concentrations. This minor effect of the clay concentration on the aluminum consumption can be attributed to the active precipitation of the colloidal aluminum hydroxide in the suspension. Practically, these appear as straight lines which may simply demonstrate the increasing tendency of the precipitation of the aluminum hydroxide corresponding to the increase in the dosage of aluminum sulfate. Therefore, instead of the effect of aluminum adsorption, the rate of precipitation of the aluminum hydroxide is the major controlling factor in the process of destabilization at this pH value. This theory is supported by the work of Packham.[18] Figure 47 shows the aluminum residual as a percentage of the aluminum added, after the separation of the colloidal aluminum hydroxides by centrifugation.

There is an inflection point in each of the electrophoretic

mobility curves shown in Figure 46 at a low aluminum sulfate dosage. This particular point of inflection seems to mark the first effect of the colloidal aluminum hydroxide on the mobility value when compared with the aluminum residual curve shown in Figure 47. At dosages higher than that at the inflection point, the mobilities reach a constant value, very close to zero, but either positive or negative, depending on the clay concentration. This slightly positive or negative value of floc mobility probably is due to the small net charge remaining on the floc as a result of a mutual coagulation between clay particles and aluminum hydroxide colloids. Consequently, the sign of the mobility value may be determined by the clay concentration in the suspension, with positive values for suspensions with very low concentrations of clay particles, while for suspensions with high concentrations of clay particles the mobility values always show zero or slightly negative values. This phenomenon was repeatedly shown in the previous electrophoretic studies of coagulation by Black and his associates.[14, 28]

The results of the measurements of the residual turbidity values as depicted in Figure 46 show that in the aluminum sulfate dosage range from 10 mg/l to 40 mg/l the initial clay concentration has an important effect on the removal of turbidity, whereas in the ranges below 10 mg/l or above 40 mg/l the clay concentration has little effect. The mechanism of physical enmeshment in destabilizing the clay suspension as proposed by Packham[19] may account for the very slight effect of the initial clay concentration at aluminum sulfate dosages higher than 40 mg/l at pH 8. However, mutual coagulation is a better mechanism

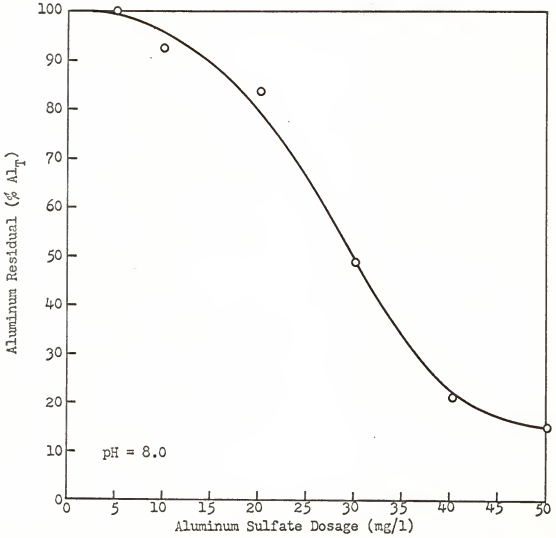

Fig. 47 - The Effect of Initial Aluminum Concentration on Aluminum Residual After Separation by High-Speed Centrifuge.

to describe the destabilization phenomena at intermediate dosages of aluminum sulfate at this pH.

Kinetics of Aluminum-Clay Interactions

Aluminum Adsorption Rate

The investigation of the aluminum adsorption rate was carried out at a constant final pH value of 5 with the temperature maintained at 25°C. The concentration of the kaolinite clay suspension was 63.3 mg/l. An aluminum sulfate dosage of 20 mg/l (1.6 mg/l of aluminum) was added to the system.

The results as depicted in Figure 48 show that about 0.67 mg/l of total aluminum, which was equal to 41.9 per cent of the total added aluminum, was adsorbed by the kaolinite clay particles during the first one minute after the addition of the aluminum sulfate to the suspension. The adsorption increased slightly with time. At the end of a 60-minute period, the adsorption value was 0.76 mg/l which was equal to 47.5 per cent of the added aluminum ion concentration. Therefore, the adsorption of aluminum hydrolysis products, which are proposed to be actively formed at this pH, can be demonstrated to be a rapid process.

Effect of Mixing Time on Residual Turbidity

In Figures 49 to 54, the residual turbidity was plotted against the total number of paddle resolutions at which the turbidity measurements were made. The total number of paddle revolutions is computed from the total time of mixing (in minutes) and the mixing rate (in

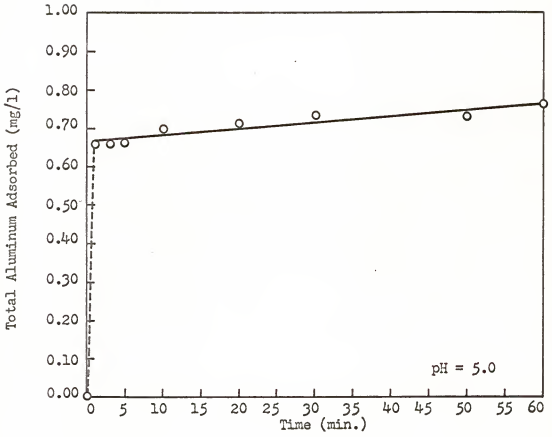

Fig. 48 - The Effect of Time on the Adsorption of Aluminum by Kaolinite Clay Particles. Initial Aluminum Concentration = 1.6 mg/l. Clay Concentration = 63.3 mg/l.

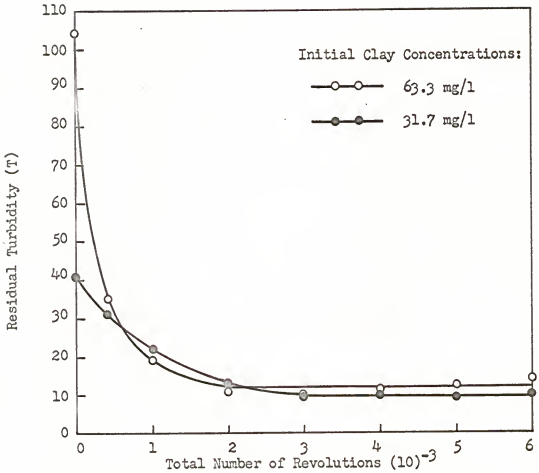

Fig. 49 - The Effect of Time of Mixing, Expressed as Total Number of Paddle Revolutions, on the Destabilization of Two Kaolinite Clay Suspensions with 5 mg/l of Aluminum Sulfate at 40 rpm Agitation Intensity. pH = 3.0.

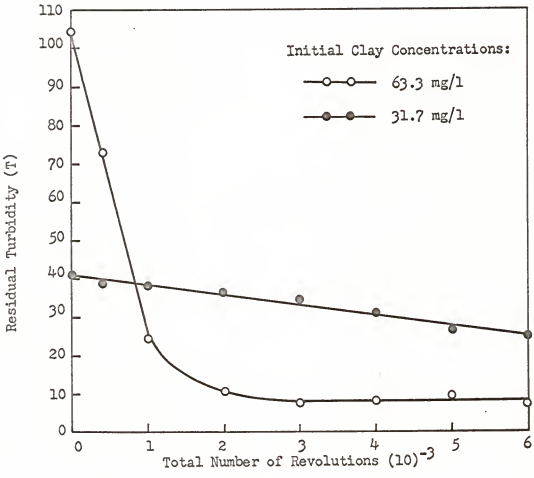

Fig. 50 - The Effect of Time of Mixing, Expressed as Total Number of Paddle Revolutions, on the Destabilization of Two Kaolinite Clay Suspensions with 5 mg/l of Aluminum Sulfate at 40 rpm Agitation Intensity. pH = 5.0 ± 0.05.

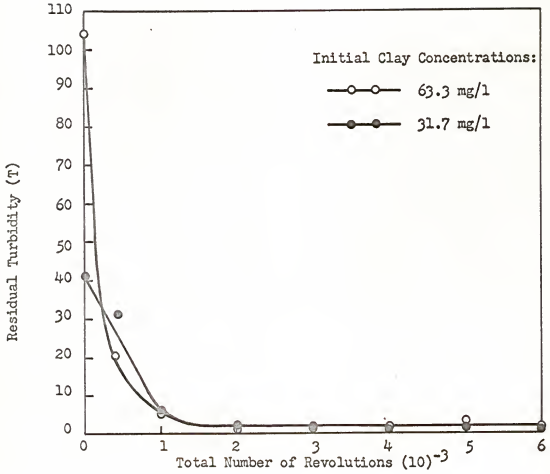

Fig. 51 - The Effect of Time of Mixing, Expressed as Total Number of Paddle Revolutions, on the Destabilization of Two Kaolinite Clay Suspensions with 30 mg/l of Aluminum Sulfate at 40 rpm Agitation Intensity. pH = 8 $\pm$ 0.1.

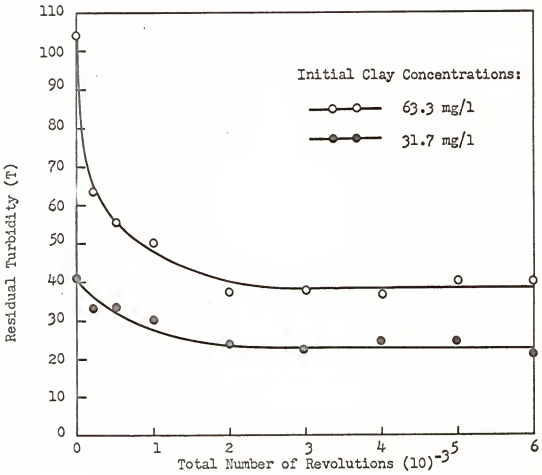

Fig. 52 - The Effect of Time of Mixing, Expressed as Total Number of Paddle Revolutions, on the Destabilization of Two Kaolinite Clay Suspensions with 5 mg/l of Aluminum Sulfate at 100 rpm Agitation Intensity. pH = 3.0.

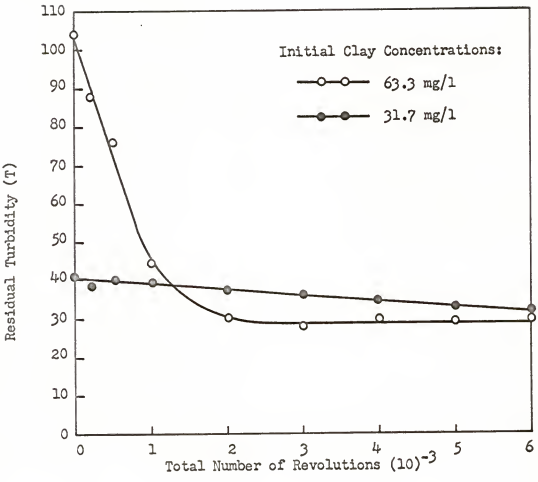

Fig. 53 - The Effect of Time of Mixing, Expressed as Total Number of Paddle Revolutions, on the Destabilization of Two Kaolinite Clay Suspensions with 5 mg/l of Aluminum Sulfate at 100 rpm Agitation Intensity. pH = 5.0 ± 0.05.

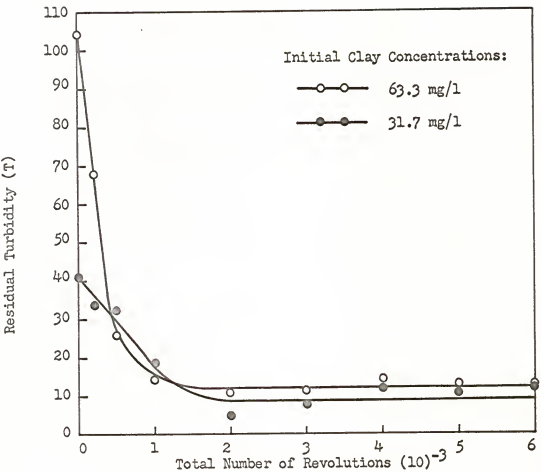

Fig. 54 - The Effect of Time of Mixing, Expressed as Total Number of Paddle Revolutions, on the Destabilization of Two Kaolinite Clay Suspensions with 30 mg/l of Aluminum Sulfate at 100 rpm Agitation Intensity. pH = 8 $\pm$ 0.1.

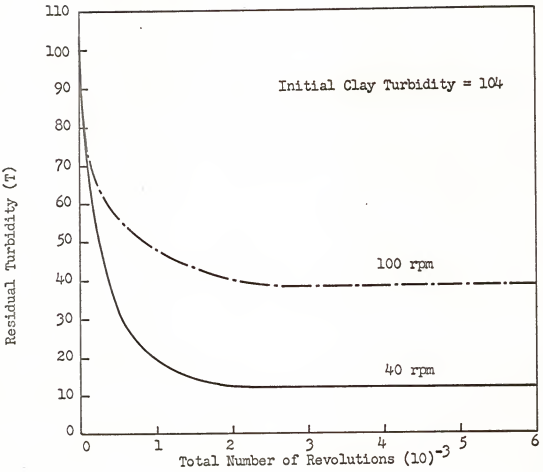

Fig. 55 - The Effect of Time of Mixing, Expressed as Total Number of Paddle Revolutions, on the Destabilization of a Kaolinite Clay Suspension with 5 mg/l of Aluminum Sulfate at Two Agitation Intensities. pH = 3.0.

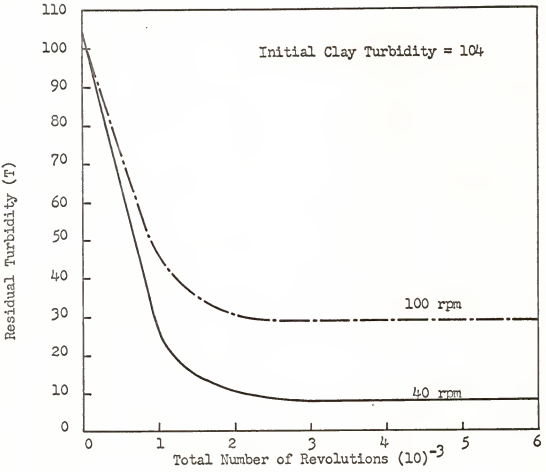

Fig. 56 - The Effect of Time of Mixing, Expressed as Total Number of Paddle Revolutions, on the Destabilization of a Kaolinite Clay Suspension with 5 mg/l of Aluminum Sulfate at Two Agitation Intensities. pH = 5.0 $\pm$ 0.05.

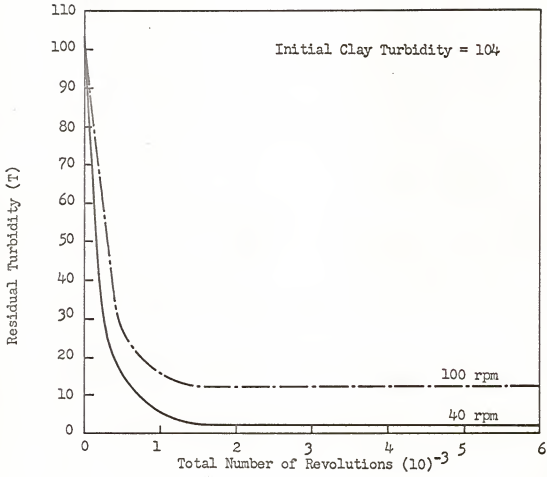

Fig. 57 - The Effect of Time of Mixing, Expressed as Total Number of Paddle Revolutions, on the Destabilization of a Kaolinite Clay Suspension with 30 mg/l of Aluminum Sulfate at Two Agitation Intensities. pH = 8 $\pm$ 0.1.

revolutions per minute).

It is clearly demonstrated that the residual turbidity curves in all cases investigated reached a constant minimum value when the suspension systems were stirred with a total of 2,000 paddle revolutions. However, the final constant minimum value of the residual turbidity curves appears to be dependent on such factors as the pH of the suspension, the coagulant dosage, the intensity of agitation and the clay concentration.

Since interparticle collision is a prerequisite to particle agglomeration, the initial rate of the reduction of turbidity should be very rapid as the initial number of particles is relatively high. According to this theory, the rate of the reduction of turbidity is diminished as the number of the suspended particles is reduced because of the formation of the particle agglomerates and the subsequent sedimentation of the larger flocs.

Effect of Agitation Intensity on Residual Turbidity

Two stirring rates were used in this series of kinetic experiments. Figures 55 to 57 show the results obtained from the investigations on the high clay concentration suspensions at three different pH values, namely, pH 3, pH 5 and pH 8.

In all cases, the agitation at a rate of 40 rpm was more effective in the reduction of turbidity than that at a rate of 100 rpm. The difference in the residual turbidities affected by different rates of agitation was reduced in the following order:

$$pH\ 3 > pH\ 5 > pH\ 8$$

This might be attributed to the different mechanisms involved in the destabilization processes at the three pH values investigated. At pH 3 the results of this investigation have supported an electrokinetic coagulation mechanism. Therefore, a moderate rate of mixing gives a better reduction in turbidity than a high rate of mixing, which produces greater shear forces in the fluid and thus makes the aggregated particles more susceptible to break-up action. Although a little bridging effect may be provided by the aluminum hydrolysis polynuclear complexes in the destabilization mechanism at pH 5, the aggregated particles at this pH value still cannot withstand the strong shear forces produced by a high rate of mixing. Consequently, a rather low rate of mixing is favored for better turbidity reduction at pH 5. However, the difference in the rate of mixing has a smaller effect in the reduction of turbidity at pH 8, at which pH the flocculated particles have stronger floc structures and are more resistant to break-up.

VI. SUMMARY AND CONCLUSIONS

Chemical grade aluminum sulfate at concentrations up to 50 mg/l was used as a coagulant to investigate the mechanisms involved in the destabilization of dilute kaolinite clay suspensions at various clay concentrations and over a pH range from 3 to 10.

Within the aluminum sulfate concentration limits used in this investigation, the pH range from 3 to 10 can be roughly divided into four different regions in which different predominant aluminum species are present. In the region below pH 4, the hydrated metallic aluminum ion is the most active aluminum species, while in the region between pH 4 and pH 6 a hydrolyzed aluminum polynuclear complex, such as $Al_6(OH)_{15}^{+++}$, $Al_7(OH)_{17}^{++++}$, $Al_8(OH)_{20}^{++++}$ and $Al_{13}(OH)_{34}^{+++++}$, is the predominant aluminum species. In the neutral pH range roughly from 6 to 8, colloidal aluminum hydroxide is the main aluminum species, while the aluminate ion, $Al(OH)_4^-$, is the predominant species in the region above pH 8.

Three major experimental approaches were used to elucidate the mechanisms involved in the specific aluminum-clay interactions with the subsequent destabilization of the clay suspensions. They were conducted in the following ways:

1. In one series, the dosage of aluminum sulfate was maintained at some selected constant value while the pH was varied.

2. In another series, the final pH value of the suspension was

maintained at a constant value of 3, 5 or 8. The choice of these three particular pH values was based on both the available literature of aqueous aluminum chemistry and the experimental results obtained from the first approach above. In this series, the aluminum sulfate dosage was varied.

3. In the series of kinetic studies, both the time of mixing and the intensity of agitation were varied.

According to the experimental results obtained, several important and significant conclusions can be drawn as follows:

1. The mechanism involved in the destabilization of the kaolinite clay suspension at pH 3 is due to a reduction of the repulsive potential between the negatively charged clay particles through a compression of the double layer. This is due to the incorporation of hydrogen and hydrated aluminum ions into the Gouy diffuse layer.

2. The destabilization of kaolinite clay suspensions at pH 5 can be attributed to a reduction of the zeta potential of the clay particles through the specific adsorption of the hydrolyzed multivalent aluminum polynuclear complex ions onto the clay surface with the subsequent reduction of the surface potential of the clay particles.

3. Physical enmeshment may account for the destabilization of kaolinite clay suspensions at pH 8 where rapid and abundant precipitation of aluminum hydroxides occurs. However, when the dosage of aluminum sulfate is less than 40 mg/l at this pH, a mechanism of mutual coagulation between colloidal aluminum hydroxides and clay particles better describes the phenomena of the destabilization.

4. The Freundlich adsorption isotherm model was found best to describe the adsorption of the hydrolyzed aluminum polynuclear complex ions by the kaolinite clay particles.

5. The residual turbidity curve as a function of the time of mixing shows that the turbidity can be reduced to a constant minimum value by stirring the suspension system with a total of 2,000 paddle revolutions.

6. The constant minimum value of the residual turbidity curve appears to be dependent on such factors as the pH of the suspension, the coagulant dosage, the intensity of agitation and the clay concentration.

7. The effect of the initial clay concentration on the destabilization process was found to follow Smoluchowski's theory at pH 3 and pH 5, whereas it had little effect at pH 8 when the aluminum sulfate dosage was higher than 50 mg/l.

APPENDIX

Table 8

The Destabilization of a Kaolinite Clay Suspension with a Dosage of 3 mg/l of Aluminum Sulfate. Initial Clay Concentration = 61.5 mg/l.

Final pH of Destabilized Suspension	HCl Added (meq/l)	NaOH Added (meq/l)	Residual Turbidity as per cent of * Initial Turbidity	Residual Aluminum (mg/l)	Final pH of Mobility Sample	Electrophoretic Mobility (μ/sec/v/cm)
2.92	1.47		15	0.24	2.92	-1.00
3.06	0.98		22	0.23	3.09	-1.00
4.14	0.07		75	0.20	4.12	-0.88
4.57	0.03		80	0.18	4.49	-0.68
4.74	0.02		83	0.16	4.72	-0.61
4.83	0.01		83	0.14	4.80	-0.72
4.98	0.00		83	0.10	4.98	-0.70
5.43		0.02	89	0.02	5.52	-1.34
5.90		0.03	89	0.00	5.94	-1.94
6.59		0.04	82	0.01	6.54	-2.29
6.62		0.04	64	0.01	6.68	-2.18
7.14		0.06	95	0.05	7.13	-2.72
8.50		0.08	93	0.21	8.49	-2.63
8.65		0.09	89	0.23	8.65	-2.40

*Initial turbidity of the suspension = 102.

Table 9

The Destabilization of a Kaolinite Clay Suspension with a Dosage of 5 mg/l of Aluminum Sulfate. Initial Clay Concentration = 61.5 mg/l.

Final pH of Destabilized Suspension	HCl Added (meq/l)	NaOH Added (meq/l)	Residual Turbidity as per cent of * Initial Turbidity	Residual Aluminum (mg/l)	Final pH of Mobility Sample	Electrophoretic Mobility (μ/sec/v/cm)
3.07	0.98		19	0.38	3.11	-0.72
3.37	0.49		48	0.37	3.36	-0.78
4.23	0.06		71	0.37	4.28	-0.78
4.55	0.03		77	0.34	4.60	-0.61
4.85	0.00		74	0.24	4.87	-0.46
4.94		0.01	83	0.17	--	--
5.25		0.03	80	0.05	--	--
5.45		0.03	89	0.05	5.40	0.59
---		0.04	--	--	5.69	1.49
6.17		0.05	83	0.02	--	--
6.45		0.06	92	0.00	--	--
6.50		0.06	89	0.04	6.44	-0.59

Table 9 - Continued

Final pH of Destabilized Suspension	HCl Added (meq/l)	NaOH Added (meq/l)	Residual Turbidity as per cent of * Initial Turbidity	Residual Aluminum (mg/l)	Final pH of Mobility Sample	Electrophoretic Mobility (μ/sec/v/cm)
7.00		0.08	75	0.05	7.13	-0.89
7.70		0.09	90	0.34	7.60	-2.36
7.85		0.10	92	0.26	7.85	-3.08
8.45		0.11	89	0.40	8.60	-2.94
8.75		0.12	86	0.40	8.90	-2.95
9.19		0.15	87	0.38	9.30	-3.01
9.44		0.17	83	0.40	9.67	-2.81
9.74		0.20	82	0.40	9.84	-3.05

*Initial turbidity of the suspension = 102.

Table 10

The Destabilization of a Kaolinite Clay Suspension with a Dosage of 7 mg/l of Aluminum Sulfate. Initial Clay Concentration = 61.5 mg/l.

Final pH of Destabilized Suspension	HCl Added (meq/l)	NaOH Added (meq/l)	Residual Turbidity as per cent of * Initial Turbidity	Residual Aluminum (mg/l)	Final pH of Mobility Sample	Electrophoretic Mobility (μ/sec/v/cm)
3.09	0.98		11	0.54	3.10	-0.69
3.52	0.34		35	0.53	3.50	-0.70
4.13	0.07		56	0.51	4.15	-0.50
4.51	0.02		67	0.49	4.54	-0.37
4.79		0.01	59	0.33	4.80	-0.28
5.09		0.03	90	0.16	5.08	1.40
5.24		0.04	90	0.10	5.24	1.74
5.29		0.05	93	0.04	5.19	1.17
5.65		0.06	95	0.06	5.69	1.54
5.82		0.06	89	0.02	--	--
6.50		0.07	82	0.01	--	--
6.70		0.07	--	0.00	6.75	0.50

Table 10 - Continued

Final pH of Destabilized Suspension	HCl Added (meq/l)	NaOH Added (meq/l)	Residual Turbidity as per cent of * Initial Turbidity	Residual Aluminum (mg/l)	Final pH of Mobility Sample	Electrophoretic Mobility (μ/sec/v/cm)
6.90		0.09	77	0.04	7.10	-1.35
7.60		0.10	76	0.06	7.60	-2.36
7.77		0.12	--	0.20	7.77	-3.66
8.50		0.13	85	0.33	8.50	-4.21
8.90		0.15	83	0.42	8.90	-3.90

*Initial turbidity of the suspension = 102.

Table 11

The Destabilization of a Kaolinite Clay Suspension with a Dosage of 10 mg/l of Aluminum Sulfate. Initial Clay Concentration = 61.5 mg/l.

Final pH of Destabilized Suspension	HCl Added (meq/l)	NaOH Added (meq/l)	Residual Turbidity as per cent of * Initial Turbidity	Residual Aluminum (mg/l)	Final pH of Mobility Sample	Electrophoretic Mobility (μ/sec/v/cm)
3.05	0.98		16	0.78	3.10	-0.21
3.57	0.29		42	0.77	3.56	-0.39
3.99	0.10		48	0.80	4.02	-0.44
4.51	0.02		59	0.71	4.53	-0.26
4.80		0.03	72	0.40	4.85	0.85
4.90		0.05	79	0.26	4.97	1.73
4.98		0.06	82	0.21	5.09	1.89
5.20		0.07	80	0.15	5.30	1.93
5.78		0.08	98	0.18	5.78	1.25
6.10		0.09	98	0.13	6.17	1.20
6.47		0.10	90	0.09	6.33	0.73
6.83		0.11	95	0.06	6.77	0.52

Table 11 - Continued

Final pH of Destabilized Suspension	HCl Added (meq/l)	NaOH Added (meq/l)	Residual Turbidity as per cent of * Initial Turbidity	Residual Aluminum (mg/l)	Final pH of Mobility Sample	Electrophoretic Mobility (μ/sec/v/cm)
7.33		0.12	75	0.16	7.10	0.50
7.66		0.13	65	--	7.30	0.58
7.70		0.14	57	0.18	7.70	-1.59
8.64		0.16	85	0.43	8.64	-4.62
9.00		0.19	86	0.68	--	--
9.00		0.20	84	0.68	9.19	-2.95
9.74		0.23	80	0.74	9.72	-1.75
9.92		0.27	79	0.80	--	--
10.05		0.30	77	0.80	10.08	-2.76
10.22		0.37	75	0.80	10.26	-3.11

*Initial turbidity of the suspension = 102.

Table 12

The Destabilization of a Kaolinite Clay Suspension with a Dosage of 15 mg/l of Aluminum Sulfate. Initial Clay Concentration = 61.5 mg/l.

Final pH of Destabilized Suspension	HCl Added (meq/l)	NaOH Added (meq/l)	Residual Turbidity as per cent of * Initial Turbidity	Residual Aluminum (mg/l)	Final pH of Mobility Sample	Electrophoretic Mobility (μ/sec/v/cm)
3.09	0.98		20	1.20	3.12	-0.48
3.68	0.25		70	1.20	3.64	-0.72
4.04	0.10		57	1.18	4.03	-0.12
4.44	0.02		73	1.17	4.38	0.00
4.90		0.07	97	0.51	4.85	1.70
5.08		0.10	97	0.47	5.08	1.71
5.59		0.13	96	0.43	--	--
5.89		0.13	89	0.48	--	--
--		0.13	--	--	5.75	1.38
6.20		0.13	98	0.38	6.20	1.06
6.24		0.14	89	0.42	6.14	0.62
6.45		0.15	97	0.29	6.46	0.45

Table 12 - Continued

Final pH of Destabilized Suspension	HCl Added (meq/l)	NaOH Added (meq/l)	Residual Turbidity as per cent of Initial Turbidity*	Residual Aluminum (mg/l)	Final pH of Mobility Sample	Electrophoretic Mobility (μ/sec/v/cm)
6.51		0.15	98	0.40	6.60	1.20
6.98		0.16	83	0.26	--	--
7.42		0.17	49	0.36	--	--
7.95		0.20	33	0.54	7.97	-0.50
7.98		0.20	30	0.48	7.96	0.77
8.27		0.22	91	0.80	8.20	-3.35
9.30		0.25	79	1.08	9.40	-2.77
9.50		0.27	77	--	9.50	-2.46
9.66		0.20	77	--	9.67	-2.36
9.82		0.32	77	1.16	9.86	-2.46

*Initial turbidity of the suspension = 102.

Table 13

The Destabilization of a Kaolinite Clay Suspension with a Dosage of 20 mg/l of Aluminum Sulfate. Initial Clay Concentration = 61.5 mg/l.

Final pH of Destabilized Suspension	HCl Added (meq/l)	NaOH Added (meq/l)	Residual Turbidity as per cent of * Initial Turbidity	Residual Aluminum (mg/l)	Final pH of Mobility Sample	Electrophoretic Mobility (μ/sec/v/cm)
3.08	0.98		16	1.60	3.10	-0.48
3.65	0.25		67	1.60	3.63	-0.47
4.04	0.10		67	1.59	4.05	-0.20
4.52	0.01		77	1.55	4.48	0.00
4.82		0.10	94	0.83	4.77	1.32
5.02		0.13	98	0.81	5.00	1.28
5.22		0.14	98	0.77	5.15	1.26
5.54		0.16	98	0.75	5.60	1.17
6.10		0.18	92	0.78	6.03	0.82
6.80		0.19	97	0.56	6.90	1.10
6.90		0.20	93	0.78	6.76	1.14
7.41		0.22	84	0.44	7.09	1.05
7.80		0.24	62	0.52	7.80	0.83
8.20		0.27	40	0.88	8.27	-1.08
--		0.29	--	--	8.18	-2.10

Table 13 - Continued

Final pH of Destabilized Suspension	HCl Added (meq/l)	NaOH Added (meq/l)	Residual Turbidity as per cent of Initial Turbidity*	Residual Aluminum (mg/l)	Final pH of Mobility Sample	Electrophoretic Mobility (μ/sec/v/cm)
8.50		0.29	89	1.32	8.30	-3.86
8.71		0.30	81	1.26	8.78	-2.70
9.35		0.35	88	1.52	9.30	-3.82
9.36		0.35	82	1.46	9.31	-3.73
9.46		0.36	75	1.20	9.62	-2.70
10.00		0.45	75	1.64	9.99	-2.76

*Initial turbidity of the suspension = 102.

Table 14

The Destabilization of a Kaolinite Clay Suspension with a Dosage of 30 mg/l of Aluminum Sulfate. Initial Clay Concentration = 61.5 mg/l.

Final pH of Destabilized Suspension	HCl Added (meq/l)	NaOH Added (meq/l)	Residual Turbidity as per cent of * Initial Turbidity	Residual Aluminum (mg/l)	Final pH of Mobility Sample	Electrophoretic Mobility (μ/sec/v/cm)
3.09	0.98		16	2.40	3.12	-0.31
3.64	0.25		49	2.40	3.62	-0.22
4.02	0.10		68	2.27	4.01	0.00
4.42	0.01		76	2.15	4.39	0.16
4.81		0.15	89	1.37	4.76	1.40
4.89		0.17	91	1.33	4.88	1.39
5.00		0.20	91	1.29	4.97	1.30
5.28		0.22	90	1.19	5.22	1.33
5.69		0.25	89	1.38	5.63	1.32
6.10		0.26	94	1.36	6.30	0.79
6.47		0.27	95	1.10	6.29	1.10
6.96		0.30	87	0.78	6.86	1.03

Table 14 - Continued

Final pH of Destabilized Suspension	HCl Added (meq/l)	NaOH Added (meq/l)	Residual Turbidity as per cent of * Initial Turbidity	Residual Aluminum (mg/l)	Final pH of Mobility Sample	Electrophoretic Mobility (μ/sec/v/cm)
7.62		0.33	11	0.44	7.55	0.52
7.68		0.33	27	0.38	7.50	0.76
7.93		0.35	14	0.60	8.06	0.00
8.20		0.38	10	1.16	8.24	-0.65
9.10		0.45	78	2.08	9.05	-3.11
9.70		0.50	76	2.18	9.74	-3.02
10.02		0.60	71	2.40	10.10	-3.19

*Initial turbidity of the suspension = 102.

Table 15

The Destabilization of a Kaolinite Clay Suspension with a Dosage of 50 mg/l of Aluminum Sulfate. Initial Clay Concentration = 61.5 mg/l.

Final pH of Destabilized Suspension	HCl Added (meq/l)	NaOH Added (meq/l)	Residual Turbidity as per cent of * Initial Turbidity	Residual Aluminum (mg/l)	Final pH of Mobility Sample	Electrophoretic Mobility (μ/sec/v/cm)
3.09	0.98		24	3.88	3.10	-0.34
3.61	0.27		60	3.93	3.60	-0.16
4.00	0.10		66	3.79	4.00	0.00
4.42	0.00		77	3.49	4.36	0.14
4.70		0.22	91	2.64	4.64	1.34
4.80		0.27	88	2.44	4.72	1.26
4.90		0.32	91	2.29	4.83	1.29
5.13		0.37	88	1.99	5.09	1.22
5.49		0.40	88	1.98	5.31	1.20
5.91		0.42	82	1.38	6.00	1.14
6.53		0.45	67	0.18	6.28	0.70
7.20		0.47	6	0.13	6.72	1.03

Table 15 - Continued

Final pH of Destabilized Suspension	HCl Added (meq/l)	NaOH Added (meq/l)	Residual Turbidity as per cent of * Initial Turbidity	Residual Aluminum (mg/l)	Final pH of Mobility Sample	Electrophoretic Mobility (μ/sec/v/cm)
7.45		0.50	4	0.38	7.21	0.90
7.83		0.52	3	0.68	7.83	0.00
8.10		0.55	5	1.23	7.98	-0.22
8.21		0.57	7	1.73	8.20	-0.69
8.43		0.65	73	3.23	8.30	-1.62
8.92		0.67	71	3.45	9.00	-3.29
9.20		0.72	77	4.00	9.48	-3.55
10.02		0.80	73	3.75	10.02	-3.31
10.22		0.87	73	3.60	10.25	-3.20

*Initial turbidity of the suspension = 102.

Table 16

Adsorption Data for Freundlich Isotherm Plot.*
Kaolinite Clay Concentration = 61.5 mg/l. pH = 4.0.

X (mg/l)	$X/M\ (10)^3$	$C\ (mg/l)(10)^3$	Log X/M	Log C
0.05	0.813	190	-3.09	-0.72
0.05	0.813	350	-3.09	-0.46
0.06	0.976	500	-3.01	-0.30
0.07	1.138	730	-2.94	-0.14
0.06	0.976	1140	-3.01	0.06
0.08	1.301	1520	-2.89	0.18
0.08	1.301	2320	-2.89	0.37
0.20	3.252	3800	-2.49	0.58

*The form of the Freundlich isotherm used is $X/M = kC^{1/n}$ or $\log X/M = (\frac{1}{n}) \log C + \log k$.

Table 17

Adsorption Data for Freundlich Isotherm Plot.*
Kaolinite Clay Concentration = 61.5 mg/l. pH = 4.5.

X (mg/l)	X/M $(10)^3$	C (mg/l)$(10)^3$	Log X/M	Log C
0.08	1.301	160	-2.89	-0.80
0.09	1.463	310	-2.83	-0.51
0.16	2.602	400	-2.58	-0.40
0.16	2.602	640	-2.58	-0.19
0.24	3.902	960	-2.41	-0.02
0.24	3,902	1360	-2.41	0.13
0.30	4.878	2100	-2.31	0.32
0.64	10.407	3360	-1.98	0.53

*The form of the Freundlich isotherm used is $X/M = kC^{1/n}$ or $\log X/M = (\frac{1}{n}) \log C + \log k$.

Table 18

Adsorption Data for Freundlich Isotherm Plot.*
Kaolinite Clay Concentration = 61.5 mg/l. pH = 5.0.

X (mg/l)	X/M $(10)^3$	C (mg/l)$(10)^3$	Log X/M	Log C
0.16	2.602	80	-2.58	-1.10
0.24	3.902	160	-2.41	-0.80
0.40	6.504	160	-2.19	-0.80
0.66	10.732	140	-1.97	-0.85
0.80	13.008	400	-1.89	-0.40
0.90	14.634	700	-1.83	-0.15
1.12	18.211	1280	-1.74	0.10
1.84	29.919	2160	-1.52	0.33

*The form of the Freundlich isotherm used is $X/M = kC^{1/n}$ or $\log X/M = (\frac{1}{n}) \log C + \log k$.

Table 19

Effect of pH on Aluminum Residual.
Kaolinite Clay Concentration = 61.5 mg/l.

pH	Total Aluminum Added (mg/l)							
	0.24	0.40	0.56	0.80	1.20	1.60	2.40	4.00
	Fraction of Aluminum Remaining in Solution							
3.0	0.980	0.950	1.000	1.000	1.000	1.000	1.000	0.990
3.5	0.917	0.925	0.982	0.975	0.983	0.987	1.000	0.990
4.0	0.792	0.875	0.893	0.912	0.950	0.950	0.967	0.950
4.5	0.667	0.775	0.714	0.800	0.800	0.850	0.875	0.840
5.0	0.334	0.400	0.286	0.175	0.334	0.437	0.533	0.540
5.5	0.042	0.025	0.054	0.150	0.292	0.375	0.517	0.445
6.0	0.000	0.000	0.036	0.200	0.383	0.412	0.567	0.300
6.5	0.021	0.000	0.036	0.112	0.267	0.431	0.500	0.060
7.0	0.125	0.012	0.036	0.100	0.217	0.350	0.317	0.000
7.5	0.417	0.437	0.143	0.200	0.283	0.250	0.175	0.080
8.0	0.687	0.837	0.393	0.400	0.458	0.400	0.267	0.240
8.5	0.896	0.950	0.643	0.600	0.717	0.750	0.667	0.762
9.0	1.000	1.000	0.804	0.800	0.850	0.881	0.842	0.920
9.5	1.000	1.000	0.929	0.912	0.942	0.950	0.933	0.950
10.0	1.000	1.000	1.000	0.987	0.983	0.994	0.996	0.970

Table 20

Construction of Formation Function Curve for Aluminum Sulfate Solution.* $Al_T = 1.5 \times 10^{-4}$ M.

pH	$[H^+]$ (mole/l)	$[OH^-]$ (mole/l)	$[Na^+]$ (mole/l)(10)	6	$[H^+]+[Na^+]-[OH^-]$ (mole/l)(10)	$\bar{n} = \frac{[OH^-]\text{ bound}}{[Al_T]}$
4.40	4.0×10^{-5}	2.5×10^{-10}	0		40	0.267
4.46	3.5×10^{-5}	2.9×10^{-10}	10		45	0.300
4.54	2.9×10^{-5}	3.5×10^{-10}	30		59	0.393
4.60	2.5×10^{-5}	4.0×10^{-10}	49		74	0.493
4.62	2.4×10^{-5}	4.2×10^{-10}	79		103	0.687
4.66	2.2×10^{-5}	4.6×10^{-10}	110		132	0.880
4.70	2.0×10^{-5}	5.0×10^{-10}	195		215	1.433
4.86	1.4×10^{-5}	7.2×10^{-10}	323		337	2.247
4.91	1.2×10^{-5}	8.1×10^{-10}	359		371	2.473
5.01	9.8×10^{-6}	1.0×10^{-9}	377		387	2.580
5.10	7.9×10^{-6}	1.3×10^{-9}	389		397	2.647
5.20	6.3×10^{-6}	1.6×10^{-9}	399		405	2.700
5.26	5.5×10^{-6}	1.8×10^{-9}	403		409	2.727
5.33	4.7×10^{-6}	2.1×10^{-9}	408		413	2.753
5.40	4.0×10^{-6}	2.5×10^{-9}	411		415	2.767
5.54	2.9×10^{-6}	3.5×10^{-9}	417		420	2.800
5.61	2.5×10^{-6}	4.1×10^{-9}	420		423	2.820
5.80	1.6×10^{-6}	6.3×10^{-9}	426		428	2.853

Table 20- Continued

pH	$[H^+]$ (mole/l)	$[OH^-]$ (mole/l)	$[Na^+]$ (mole/l)(10)^6	$[H^+]+[Na^+]-[OH^-]$ (mole/l)(10)^6	$\bar{n} = \frac{[OH^-]\text{ bound}}{[Al_T]}$
6.00	1.0×10^{-6}	1.0×10^{-8}	430	431	2.873
6.21	6.2×10^{-7}	1.6×10^{-8}	435	436	2.907
6.36	4.4×10^{-7}	2.3×10^{-8}	439	439	2.927
6.48	3.3×10^{-7}	3.0×10^{-8}	443	443	2.953
6.60	2.5×10^{-7}	4.0×10^{-8}	447	447	2.980
6.72	1.9×10^{-7}	5.2×10^{-8}	450	450	3.000
6.86	1.4×10^{-7}	7.2×10^{-8}	454	454	3.027
6.96	1.1×10^{-7}	9.1×10^{-8}	460	460	3.067
7.06	8.7×10^{-8}	1.1×10^{-7}	464	464	3.093
7.19	6.5×10^{-8}	1.5×10^{-7}	470	470	3.133
7.25	5.6×10^{-8}	1.8×10^{-7}	474	474	3.160
7.35	4.5×10^{-8}	2.2×10^{-7}	479	479	3.193
7.42	3.8×10^{-8}	2.6×10^{-7}	485	485	3.233
7.51	3.1×10^{-8}	3.2×10^{-7}	490	490	3.267
7.57	2.7×10^{-8}	3.7×10^{-7}	495	495	3.300
7.72	1.9×10^{-8}	5.2×10^{-7}	505	505	3.367
7.82	1.5×10^{-8}	6.6×10^{-7}	516	516	3.440
7.92	1.2×10^{-8}	8.3×10^{-7}	527	527	3.513
8.02	9.5×10^{-9}	1.0×10^{-6}	538	537	3.580
8.12	7.6×10^{-9}	1.3×10^{-6}	555	554	3.693
8.26	5.5×10^{-9}	1.8×10^{-6}	578	576	3.840

Table 20 - Continued

pH	$[H^+]$ (mole/l)	$[OH^-]$ (mole/l)	$[Na^+]$ (mole/l)(10)^6	$[H^+]+[Na^+]-[OH^-]$ (mole/l)(10)^6	$\bar{n} = \frac{[OH^-]_{bound}}{[Al_T]}$
8.33	4.7×10^{-9}	2.1×10^{-6}	598	596	3.973
8.40	4.0×10^{-9}	2.5×10^{-6}	625	622	4.147
8.72	1.9×10^{-9}	5.2×10^{-6}	687	682	4.547
9.08	8.3×10^{-10}	1.2×10^{-5}	708	696	4.640
9.37	4.3×10^{-10}	2.3×10^{-5}	730	707	4.713
9.57	2.7×10^{-10}	3.7×10^{-5}	758	721	4.807
9.71	1.9×10^{-10}	5.1×10^{-5}	781	730	4.867
9.84	1.4×10^{-10}	6.9×10^{-5}	809	740	4.933
9.91	1.2×10^{-10}	8.1×10^{-5}	833	752	5.013
10.08	8.3×10^{-11}	1.2×10^{-4}	890	770	5.133
10.35	4.5×10^{-11}	2.2×10^{-4}	1036	816	5.440
10.57	2.7×10^{-11}	3.7×10^{-4}	1262	892	5.947

*Temperature = (25 ± 0.5)°C.

Table 21

The Effect of Total Number of Paddle Revolutions and Intensity of Agitation upon the Destabilization of a Kaolinite Clay Suspension with Aluminum Sulfate.* Initial Clay Concentration = 63.3 mg/l. pH = 3.0

Intensity of Agitation, 40 rpm		Intensity of Agitation, 100 rpm	
Total Number of Revolutions	Residual Turbidity	Total Number of Revolutions	Residual Turbidity
0	104	0	104
400	35	200	64
1000	19	500	56
2000	11	1000	50
3000	10	2000	37
4000	12	3000	38
5000	13	4000	36
6000	15	5000	40
		6000	40

*The dosage of aluminum sulfate is 5 mg/l.

Table 22

The Effect of Total Number of Paddle Revolutions and Intensity of Agitation upon the Destabilization of a Kaolinite Clay Suspension with Aluminum Sulfate.* Initial Clay Concentration = 63.3 mg/l. pH = 5 ± 0.05

Intensity of Agitation, 40 rpm		Intensity of Agitation, 100 rpm	
Total Number of Revolutions	Residual Turbidity	Total Number of Revolutions	Residual Turbidity
0	104	0	104
400	73	200	88
1000	24	500	76
2000	11	1000	45
3000	8	2000	30
4000	8	3000	28
5000	9	4000	30
6000	7	5000	29
		6000	30

*The dosage of aluminum sulfate is 5 mg/l.

Table 23

The Effect of Total Number of Paddle Revolutions and Intensity of Agitation upon the Destabilization of a Kaolinite Clay Suspension with Aluminum Sulfate.* Initial Clay Concentration = 63.3 mg/l. pH = 8 ± 0.1

Intensity of Agitation, 40 rpm		Intensity of Agitation, 100 rpm	
Total Number of Revolutions	Residual Turbidity	Total Number of Revolutions	Residual Turbidity
0	104	0	104
400	20	200	68
1000	5	500	26
2000	1	1000	14
3000	2	2000	11
4000	2	3000	12
5000	3	4000	14
6000	2	5000	13
		6000	13

*The dosage of aluminum sulfate is 30 mg/l.

Table 24

The Effect of Total Number of Paddle Revolutions and Intensity of Agitation upon the Destabilization of a Kaolinite Clay Suspension with Aluminum Sulfate.* Initial Clay Concentration = 31.7 mg/l. pH = 3.0

Intensity of Agitation, 40 rpm		Intensity of Agitation, 100 rpm	
Total Number of Revolutions	Residual Turbidity	Total Number of Revolutions	Residual Turbidity
0	41	0	41
400	31	200	33
1000	22	500	34
2000	14	1000	30
3000	10	2000	24
4000	10	3000	22
5000	9	4000	25
6000	10	5000	24
		6000	21

*The dosage of aluminum sulfate is 5 mg/l.

Table 25

The Effect of Total Number of Paddle Revolutions and Intensity of Agitation upon the Destabilization of a Kaolinite Clay Suspension with Aluminum Sulfate.* Initial Clay Concentration = 31.7 mg/l. pH = 5 ± 0.05

Intensity of Agitation, 40 rpm		Intensity of Agitation, 100 rpm	
Total Number of Revolutions	Residual Turbidity	Total Number of Revolutions	Residual Turbidity
0	41	0	41
400	39	200	39
1000	38	500	40
2000	37	1000	40
3000	35	2000	38
4000	31	3000	37
5000	27	4000	35
6000	20	5000	33
		6000	32

*The dosage of aluminum sulfate is 5 mg/l.

Table 26

The Effect of Total Number of Paddle Revolutions and Intensity of Agitation upon the Destabilization of a Kaolinite Clay Suspension with Aluminum Sulfate.* Initial Clay Concentration = 31.7 mg/l. pH = 8 ± 0.1

Intensity of Agitation, 40 rpm		Intensity of Agitation, 100 rpm	
Total Number of Revolutions	Residual Turbidity	Total Number of Revolutions	Residual Turbidity
0	41	0	41
400	31	200	34
1000	6	500	33
2000	2	1000	19
3000	2	2000	5
4000	1	3000	8
5000	2	4000	12
6000	2	5000	11
		6000	12

*The dosage of aluminum sulfate is 30 mg/l.

Table 27

The Effect of pH on Aluminum Residual After Separation by High-Speed Centrifuge.* Initial Aluminum Concentration = 4.00 mg/l.

	Aluminum Residual	
pH	As mg/l	As Percent of Initial Concentration
3.01	3.98	99.4
4.00	3.99	99.9
4.61	3.90	97.5
5.10	3.25	87.3
5.61	3.00	75.0
5.96	2.61	65.1
6.57	2.11	52.6
6.68	1.31	32.8
7.44	0.38	9.4
7.96	1.03	25.8
8.67	3.75	93.8
9.18	3.95	98.8
10.10	3.98	99.4

*With a speed of 9,000 rpm and a period of 10 minutes.

Table 28

The Effect of Aluminum Concentration on Aluminum Residual After Separation by High-Speed Centrifuge.* pH = 8.0.

Initial Aluminum Concentration (mg/l)	Aluminum Residual	
	As mg/l	As Percent of Initial Concentration
0.40	0.40	100
0.80	0.75	92.6
1.60	1.34	83.8
2.40	1.18	48.8
3.20	0.68	21.1
4.00	0.60	15.0

*With a speed of 9,000 rpm and a period of 10 minutes.

Table 29

The Effect of Time on the Adsorption of Aluminum by Kaolinite Clay. Clay Concentration = 63.3 mg/l. Aluminum Dosage = 1.60 mg/l.

pH = 5.0		Temp. = 25°C.
Time (Min.)	Aluminum Residual (mg/l)	Aluminum Adsorbed (mg/l)
0	1.60	0.00
1	0.94	0.66
3	0.94	0.66
5	0.94	0.66
10	0.90	0.70
20	0.89	0.71
30	0.87	0.73
50	0.87	0.73
60	0.84	0.76

Table 30

The Effect of pH on the Electrophoretic Mobility of Kaolinite Clay Particle.* Clay Concentration = 63.3 mg/l.

pH of Suspension	HCl Added (meq/l)	NaOH Added (meq/l)	Electrophoretic Mobility (μ/sec/v/cm)
3.14	1.37		-2.96
3.77	0.78		-2.67
4.34	0.64		-2.83
5.22	0.57		-2.88
5.74	0.49		-2.90
6.23	0.34		-2.99
6.69	0.20		-2.91
7.04	0.10		-3.02
7.78	0.00		-3.00
8.30		0.03	-3.12
8.76		0.06	-3.16
9.12		0.10	-2.91
9.52		0.20	-3.19
10.07		0.50	-3.34

*A total of 50 ppm $NaHCO_3$ was added to the suspension before the pH was adjusted with 0.1 N HCl or 0.1 N NaOH.

Table 31

The Zone of Aluminum Floc Formation.*

Temperature = 25°C.

Concentration of Aluminum (mole/liter)	Low pH Limit	High pH Limit	Presence of Visible Floc
1.0×10^{-3}	4.40	9.20	Yes
5.0×10^{-4}	4.50	8.90	Yes
3.0×10^{-4}	4.55	8.90	Yes
1.5×10^{-4}	4.90	8.60	Yes
1.0×10^{-4}	5.00	8.50	No
7.5×10^{-5}	6.00	8.30	No
6.0×10^{-5}	7.00	8.20	No

*The zone is defined by the evidence of Tyndall effect in aluminum sulfate solution.

Table 32

The Effect of pH and Anion on the Electrophoretic Mobility of Aluminum Floc. Aluminum Concentration = 1.5×10^{-4} M. Temp. = 25°C.

$Al_2(SO_4)_3 \cdot 18 H_2O$		$Al(NO_3)_3 \cdot 9 H_2O$		$Al(NO_3)_3 \cdot 9 H_2O$ and 2.25×10^{-4} M Na_2SO_4	
pH	Mobility (μ/sec/v/cm)	pH	Mobility (μ/sec/v/cm)	pH	Mobility (μ/sec/v/cm)
5.00	0.89	5.25	2.76	5.00	1.45
5.32	0.97	5.67	2.85	5.66	1.56
5.34	0.87	6.15	2.88	6.08	1.71
5.60	1.03	6.29	2.80	6.14	1.56
5.62	0.94	6.82	2.70	6.47	1.40
6.00	1.18	6.93	2.52	6.50	1.35
6.26	1.02	7.39	2.35	6.51	1.45
6.40	1.16	7.50	2.40	7.34	1.31
6.42	1.23	7.61	2.19	7.43	1.34
6.54	1.13	7.70	2.20	7.67	1.28
6.87	1.16	7.86	2.01	7.96	1.05
7.22	1.01	8.13	1.91	8.32	0.87
7.34	1.02	8.40	1.28	8.50	0.51
7.76	1.02	8.42	1.18		
7.91	1.01				
7.96	1.08				
8.22	0.90				
8.46	0.54				
8.58	0.74				
8.71	-0.77				

Table 33

The Effect of pH on the Electrophoretic Mobility of Kaolinite Clay Particle with a Dosage of 50 mg/l Aluminum Sulfate.* Clay concentration = 63.3 mg/l. Temperature = 25°C.

pH of Clay Suspension	NaOH Added (meq/l)	HCl Added (meq/l)	Electrophoretic Mobility (μ/sec/v/cm)
3.14		1.37	-0.41
3.72		0.78	-0.30
4.13		0.64	-0.09
4.41		0.59	0.37
4.52		0.54	1.14
4.57		0.49	1.78
4.70		0.34	1.78
5.08		0.12	1.49
5.70		0.10	1.54
6.10	0.05		1.41
6.40	0.15		1.30
6.61	0.25		1.24
6.81	0.30		1.23
6.98	0.35		1.13
8.00	0.56		0.32
8.22	0.61		0.42
9.04	0.77		-3.14
9.76	1.01		-4.09

*A total of 50 mg/l $NaHCO_3$ was added to the suspensions before the pH was adjusted with 0.1 N HCl or 0.1 N NaOH.

Table 34

Adsorption Data for Freundlich Isotherm Plot.* Kaolinite Clay
Concentration = 15.8 mg/l. pH = 5 ± 0.05. Temp. = (25 ± 0.5)°C.

X (mg/l)	X/M $(10)^3$	C (mg/l)$(10)^3$	Log X/M	Log C
0.03	1.899	50	-2.72	-1.30
0.08	5.063	170	-2.20	-0.77
0.16	10.127	240	-1.99	-0.62
0.25	15.823	310	-1.80	-0.51
0.29	18.354	520	-1.74	-0.28
0.36	22.785	1240	-1.64	0.09
0.44	27.848	1980	-1.56	0.30
0.57	36.076	2630	-1.44	0.42
1.05	66.456	2950	-1.18	0.47

*The form of the Freundlich isotherm used is $X/M = kC^{1/n}$ or $\log X/M = (\frac{1}{n}) \log C + \log k$.

Table 35

Adsorption Data for Freundlich Isotherm Plot.*
Kaolinite Clay Concentration = 31.7 mg/l.
pH = 5 ± 0.05. Temp. = (25 ± 0.5)°C.

X (mg/l)	$X/M_{(10)^3}$	C (mg/l)$(10)^3$	Log X/M	Log C
0.04	1.262	40	-2.90	-1.40
0.15	4.732	100	-2.32	-1.00
0.19	5.994	210	-2.22	-0.68
0.32	10.095	240	-2.00	-0.62
0.38	11.988	430	-1.92	-0.37
0.48	15.143	1120	-1.83	0.05
0.67	21.137	1750	-1.67	0.24
0.78	24.607	2430	-1.61	0.39
1.36	42.905	2650	-1.37	0.42

*The form of the Freundlich isotherm used is $X/M = kC^{1/n}$ or $\log X/M = (\frac{1}{n}) \log C + \log k$.

Table 36

Adsorption Data for Freundlich Isotherm Plot.*
Kaolinite Clay Concentration = 47.5 mg/l.
pH = 5 ± 0.05. Temp. = (25 ± 0.5)°C.

X (mg/l)	X/M $(10)^3$	C (mg/l)$(10)^3$	Log X/M	Log C
0.05	1.053	30	-2.98	-1.52
0.17	3.579	80	-2.45	-1.10
0.23	4.842	170	-2.31	-0.77
0.35	7.368	210	-2.13	-0.68
0.47	9.894	340	-2.00	-0.47
0.62	13.052	980	-1.88	-0.01
0.73	15.368	1690	-1.81	0.23
1.02	21.473	2180	-1.67	0.34
1.53	32.210	2470	-1.49	0.39

*The form of the Freundlich isotherm used is $X/M = kC^{1/n}$ or $\log X/M = (\frac{1}{n}) \log C + \log k$.

Table 37

Adsorption Data for Freundlich Isotherm Plot.*
Kaolinite Clay Concentration = 63.3 mg/l.
pH = 5 ± 0.05. Temp. = (25 ± 0.5)°C.

X (mg/l)	X/M $(10)^3$	C (mg/l)$(10)^3$	Log X/M	Log C
0.06	0.948	20	-3.02	-1.70
0.18	2.844	70	-2.55	-1.15
0.26	4.107	140	-2.39	-0.85
0.38	6.003	180	-2.22	-0.74
0.56	8.846	250	-2.05	-0.60
0.76	12.007	840	-1.92	-0.08
0.94	14.850	1480	-1.83	0.17
1.25	19.747	1950	-1.70	0.29
1.79	28.278	2210	-1.55	0.34

*The form of the Freundlich isotherm used is $X/M = k\, C^{1/n}$ or $\log X/M = (\frac{1}{n}) \log C + \log k$.

Table 38

The Destabilization of a Kaolinite Clay Suspension with Aluminum Sulfate.
Initial Clay Concentration = 15.8 mg/l.

Final pH = 3.0 — Temperature = (25 ± 0.5)°C

Total Aluminum Applied (mg/l)	HCl Added (meq/l)	NaOH Added (meq/l)	Residual Turbidity as per cent of * Initial Turbidity	Residual Aluminum (mg/l)	Total Aluminum Consumed (mg/l)	Electrophoretic Mobility (μ/sec/v/cm)
0.00	1.13		78	0.00	0.00	-2.49
0.08	1.13		80	0.08	0.00	-1.29
0.25	1.13		80	0.25	0.00	-0.99
0.40	1.13		83	0.40	0.00	-0.89
0.56	1.13		80	0.56	0.00	-0.73
0.81	1.13		80	0.81	0.00	-0.63
1.60	1.13		80	1.60	0.00	-0.36
2.42	1.13		83	2.41	0.01	-0.27
3.20	1.13		80	3.20	0.00	-0.27
4.00	1.13		80	4.00	0.00	-0.23

*Initial turbidity of the suspension = 20.

Table 39

The Destabilization of a Kaolinite Clay Suspension with Aluminum Sulfate.
Initial Clay Concentration = 31.7 mg/l.

Final pH = 3.0 Temperature = (25 ± 0.5)°C

Total Aluminum Applied (mg/l)	HCl Added (meq/l)	NaOH Added (meq/l)	Residual Turbidity as per cent of Initial Turbidity*	Residual Aluminum (mg/l)	Total Aluminum Consumed (mg/l)	Electrophoretic Mobility (μ/sec/v/cm)
0.00	1.13		60	0.00	0.00	-2.61
0.08	1.13		60	0.07	0.01	-1.39
0.25	1.13		60	0.25	0.00	-1.03
0.40	1.13		61	0.40	0.00	-0.91
0.56	1.13		61	0.55	0.01	-0.71
0.81	1.13		61	0.81	0.00	-0.64
1.60	1.13		61	1.60	0.00	-0.34
2.42	1.13		60	2.42	0.00	-0.28
3.20	1.13		62	3.20	0.00	-0.25
4.00	1.13		67	4.00	0.00	-0.22

*Initial turbidity of the suspension = 41.

Table 40

The Destabilization of a Kaolinite Clay Suspension with Aluminum Sulfate.
Initial Clay Concentration = 47.5 mg/l.

Final pH = 3.0 Temperature = (25 ± 0.5)°C

Total Aluminum Applied (mg/l)	HCl Added (meq/l)	NaOH Added (meq/l)	Residual Turbidity as per cent of * Initial Turbidity	Residual Aluminum (mg/l)	Total Aluminum Consumed (mg/l)	Electrophoretic Mobility (μ/sec/v/cm)
0.00	1.13		51	0.00	0.00	-2.63
0.08	1.13		50	0.05	0.03	-1.46
0.25	1.13		50	0.25	0.00	-1.12
0.40	1.13		51	0.40	0.00	-0.90
0.56	1.13		47	0.56	0.00	-0.85
0.81	1.13		50	0.80	0.01	-0.71
1.60	1.13		46	1.60	0.00	-0.34
2.42	1.13		46	2.37	0.05	-0.31
3.20	1.13		52	3.20	0.00	-0.28
4.00	1.13		52	3.95	0.05	-0.25

*Initial turbidity of the suspension = 67.

Table 41

The Destabilization of a Kaolinite Clay Suspension with Aluminum Sulfate.
Initial Clay Concentration = 63.3 mg/l.

Final pH = 3.0 Temperature = (25 ± 0.5)°C

Total Aluminum Applied (mg/l)	HCl Added (meq/l)	NaOH Added (meq/l)	Residual Turbidity as per cent of Initial Turbidity*	Residual Aluminum (mg/l)	Total Aluminum Consumed (mg/l)	Electrophoretic Mobility (μ/sec/v/cm)
0.00	1.13		29	0.00	0.00	-2.44
0.08	1.13		30	0.05	0.03	-1.39
0.25	1.13		30	0.24	0.01	-0.97
0.40	1.13		29	0.38	0.02	-0.88
0.56	1.13		28	0.53	0.03	-0.75
0.81	1.13		28	0.76	0.05	-0.65
1.60	1.13		27	1.58	0.02	-0.50
2.42	1.13		26	2.42	0.00	-0.36
3.20	1.13		26	4.00	0.00	-0.26
4.00	1.13		26	4.00	0.00	-0.26

*Initial turbidity of the suspension = 104.

Table 42

The Destabilization of a Kaolinite Clay Suspension with Aluminum Sulfate.
Initial Clay Concentration = 15.8 mg/l.
Final pH = 5 ± 0.05. Temp. = (25 ± 0.5)°C.

Total Aluminum Applied (mg/l)	HCl Added (meq/l)	NaOH Added (meq/l)	Residual Turbidity* (% T_i) I**	II***	Residual Aluminum (mg/l)	Total Aluminum Adsorbed (mg/l)	Electrophoretic Mobility (μ/sec/v/cm)
0.00	0.015		95	--	0.00	0.00	-3.27
0.08	0.010		98	100	0.05	0.03	-1.37
0.25	0.000		98	95	0.17	0.08	-0.44
0.40		0.013	98	100	0.24	0.16	1.73
0.56		0.028	98	105	0.31	0.25	1.85
0.81		0.056	95	100	0.52	0.29	1.85
1.60		0.131	98	98	1.24	0.36	1.52
2.42		0.202	93	103	1.98	0.44	1.47
3.20		0.278	88	100	2.63	0.57	1.65
4.00		0.353	88	98	2.95	1.05	1.66

*Initial turbidity (T_i) of the suspension = 20.

**With 2 minutes of rapid mixing (100 rpm) followed by 28 minutes of slow mixing (10 rpm) and 10 minutes of settlement.

***With 20 minutes of rapid mixing (100 rpm) followed by 10 minutes of slow mixing (10 rpm) and 10 minutes of settlement.

Table 43

The Destabilization of a Kaolinite Clay Suspension with Aluminum Sulfate.
Initial Clay Concentration = 31.7 mg/l.

Final pH = 5 ± 0.05 Temperature = (25 ± 0.5)°C

Total Aluminum Applied (mg/l)	HCl Added (meq/l)	NaOH Added (meq/l)	Residual Turbidity* (% T_i) I**	II***	Residual Aluminum (mg/l)	Total Aluminum Adsorbed (mg/l)	Electrophoretic Mobility (μ/sec/v/cm)
0.00	0.014		90	--	0.00	0.00	-3.25
0.08	0.009		90	94	0.04	0.04	-1.35
0.25		0.003	89	66	0.10	0.15	-0.60
0.40		0.014	93	53	0.21	0.19	0.77
0.56		0.029	95	95	0.24	0.32	1.78
0.81		0.056	93	98	0.43	0.38	1.84
1.60		0.136	93	95	1.12	0.48	1.43
2.42		0.210	91	93	1.75	0.67	1.51
3.20		0.283	87	89	2.43	0.78	1.59
4.00		0.364	88	88	2.65	1.36	1.55

*Initial turbidity (T_i) of the suspension = 41.

**With 2 minutes of rapid mixing (100 rpm) followed by 28 minutes of slow mixing (10 rpm) and 10 minutes of settlement.

***With 20 minutes of rapid mixing (100 rpm) followed by 10 minutes of slow mixing (10 rpm) and 10 minutes of settlement.

Table 44

The Destabilization of a Kaolinite Clay Suspension with Aluminum Sulfate.
Initial Clay Concentration = 47.5 mg/l.

Final pH = 5 ± 0.05 Temperature = (25 ± 0.5)°C

Total Aluminum Applied (mg/l)	HCl Added (meq/l)	NaOH Added (meq/l)	Residual Turbidity* (% T_i) I**	II***	Residual Aluminum (mg/l)	Total Aluminum Adsorbed (mg/l)	Electrophoretic Mobility (μ/sec/v/cm)
0.00	0.014		93	--	0.00	0.00	-1.75
0.08	0.009		95	93	0.03	0.05	-0.84
0.25		0.003	83	55	0.08	0.17	-0.38
0.40		0.014	84	43	0.17	0.23	0.26
0.56		0.029	89	97	0.21	0.35	1.59
0.81		0.055	90	101	0.34	0.47	1.80
1.60		0.137	92	101	0.98	0.62	1.40
2.42		0.211	90	99	1.69	0.73	1.51
3.20		0.286	87	96	2.18	1.02	1.57
4.00		0.367	88	93	2.47	1.53	1.49

*Initial turbidity (T_i) of the suspension = 67.

**With 2 minutes of rapid mixing (100 rpm) followed by 28 minutes of slow mixing (10 rpm) and 10 minutes of settlement.

***With 20 minutes of rapid mixing (100 rpm) followed by 10 minutes of slow mixing (10 rpm) and 10 minutes of settlement.

Table 45

The Destabilization of a Kaolinite Clay Suspension with Aluminum Sulfate.
Initial Clay Concentration = 63.3 mg/l.

Final pH = 5 ± 0.05 Temperature = (25 ± 0.5)°C

Total Aluminum Applied (mg/l)	HCl Added (meq/l)	NaOH Added (meq/l)	Residual Turbidity* (% T_i) I**	II***	Residual Aluminum (mg/l)	Total Aluminum Adsorbed (mg/l)	Electrophoretic Mobility (μ/sec/v/cm)
0.00	0.014		93	--	0.00	0.00	-2.44
0.08	0.009		93	84	0.02	0.06	-1.55
0.25		0.003	82	34	0.07	0.18	-0.77
0.40		0.014	65	17	0.14	0.26	-0.47
0.56		0.029	86	81	0.18	0.38	0.91
0.81		0.054	92	87	0.25	0.56	1.23
1.60		0.139	95	87	0.84	0.76	1.31
2.42		0.212	95	84	1.48	0.94	1.40
3.20		0.288	84	81	1.95	1.25	1.47
4.00		0.369	82	74	2.21	1.79	1.41

*Initial turbidity (T_i) of the suspension = 104.

**With 2 minutes of rapid mixing (100 rpm) followed by 28 minutes of slow mixing (10 rpm) and 10 minutes of settlement.

***With 20 minutes of rapid mixing (100 rpm) followed by 10 minutes of slow mixing (10 rpm) and 10 minutes of settlement.

Table 46

The Destabilization of a Kaolinite Clay Suspension with Aluminum Sulfate.
Initial Clay Concentration = 15.8 mg/l.

Final pH = 8 ± 0.1 Temperature = (25 ± 0.5)°C

Total Aluminum Applied (mg/l)	HCl Added (meq/l)	NaOH Added (meq/l)	Residual Turbidity as per cent of * Initial Turbidity	Residual Aluminum (mg/l)	Total Aluminum Consumed (mg/l)	Electrophoretic Mobility (μ/sec/v/cm)
0.00		0.043	95	0.00	0.00	-3.47
0.40		0.104	93	0.29	0.11	-3.36
0.81		0.160	93	0.41	0.40	-0.52
1.60		0.260	90	0.65	0.95	0.28
2.42		0.361	68	0.77	1.65	0.24
3.20		0.465	23	1.03	2.17	0.23
4.00		0.555	13	0.97	3.03	0.34

*Initial turbidity of the suspension = 20.

Table 47

The Destabilization of Kaolinite Clay Suspension with Aluminum Sulfate.
Initial Clay Concentration = 31.7 mg/l.

Final pH = 8 ± 0.1 Temperature = (25 ± 0.5)°C

Total Aluminum Applied (mg/l)	HCl Added (meq/l)	NaOH Added (meq/l)	Residual Turbidity as per cent of Initial Turbidity*	Residual Aluminum (mg/l)	Total Aluminum Consumed (mg/l)	Electrophoretic Mobility (μ/sec/v/cm)
0.00		0.043	93	0.00	0.00	-3.16
0.40		0.101	88	0.25	0.15	-2.72
0.81		0.154	88	0.50	0.31	-1.02
1.60		0.258	81	0.63	0.97	0.35
2.42		0.359	57	0.88	1.54	0.00
3.20		0.462	6	0.94	2.26	-0.23
4.00		0.558	5	0.85	3.15	0.00

*Initial turbidity of the suspension = 41.

Table 48

The Destabilization of a Kaolinite Clay Suspension with Aluminum Sulfate.
Initial Clay Concentration = 47.5 mg/l.

Final pH = 8 ± 0.1 Temperature = (25 ± 0.5)°C

Total Aluminum Applied (mg/l)	HCl Added (meq/l)	NaOH Added (meq/l)	Residual Turbidity as per cent of * Initial Turbidity	Residual Aluminum (mg/l)	Total Aluminum Consumed (mg/l)	Electrophoretic Mobility (μ/sec/v/cm)
0.00		0.043	91	0.00	0.00	-3.28
0.40		0.104	90	0.32	0.08	-3.36
0.81		0.160	84	0.63	0.18	-0.48
1.60		0.260	65	0.68	0.92	-0.54
2.42		0.361	25	0.76	1.66	-0.48
3.20		0.462	11	0.99	2.21	-0.53
4.00		0.555	6	1.10	2.90	-0.57

*Initial turbidity of the suspension = 67.

Table 49

The Destabilization of a Kaolinite Clay Suspension with Aluminum Sulfate.
Initial Clay Concentration = 63.3 mg/l.

Final pH = 8 ± 0.1 Temperature = (25 ± 0.5)°C

Total Aluminum Applied (mg/l)	HCl Added (meq/l)	NaOH Added (meq/l)	Residual Turbidity as per cent of Initial Turbidity*	Residual Aluminum (mg/l)	Total Aluminum Consumed (mg/l)	Electrophoretic Mobility (μ/sec/v/cm)
0.00		0.043	83	0.00	0.00	-3.47
0.40		0.104	77	0.37	0.03	-3.14
0.81		0.160	85	0.56	0.25	-2.12
1.60		0.260	33	0.68	0.92	-0.36
2.42		0.361	12	0.79	1.63	-0.36
3.20		0.462	6	1.01	2.19	-0.25
4.00		0.555	4	1.12	2.88	-0.08

*Initial turbidity of the suspension = 104.

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BIOGRAPHICAL SKETCH

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This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Engineering and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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